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#### THE

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# PHILOSOPHICAL MAGAZINE

AND

# JOURNAL OF SCIENCE.

CONDUCTED BY

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"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." Just. Lips. Polit. lib. i. cap. 1. Not.

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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua.... Admiratio generat quæstionem, quæstio investigationem investigatio inventionem."—Hugo de S. Victore.

——"Cur spirent venti, cur terra dehiscat, Cur mare turgescat, pelago cur tantus amaror, Cur caput obscura Phœbus ferrugine condat, Quid toties diros cogat flagrare cometas, Quid pariat nubes, veniant cur fulmina cœlo, Quo micet igne Iris, superos quis conciat orbes Tam vario motu."

J. B. Pinelli ad Mazonium.



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#### ERRATA IN VOL. XXVI.

- Page 168, line 4 from bottom, for e, the thickness of the lens at its centre, read ne, the thickness of the lens at its centre.
- 451, line 8 from bottom, for Figs. 7 to 14 (Pls. IV., V.) read
   Figs. 1 to 6 (Pl. IV.).
- 453, line 9 from bottom, for Figs. 8 to 14, Pl. V., read Figs. 8 and 9, Pl. V.
- 453, line 2 from bottom, after the present insert (Pl. V. fig. 10).
- 454, line 7 from above, omit the word following, and at the end of the sentence insert (Pl. V. fig. 12).

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JULY 1888.

I. On the Indices of Refraction of the Metals. By A. Kundt\*.

THE simplest, and at the same time the most reliable, method of determining indices of refraction, i.e. the relative velocities of light in transparent bodies, is that of prismatic deviation. This method has proved available even for strongly absorbent intensely-coloured substances which show considerable irregularity of dispersion in particular parts of the spectrum, if prisms of suitable form are employed. No attempt has, however, yet been made to determine the prismatic deviation of light in metals, since the metals, even in very thin films, are completely opaque. Attempts have, therefore, been made in other ways to draw conclusions as to the velocity of light in the metals. In particular the index of refraction for silver has been calculated by Quincke from various interference phenomena, and by Wernicke from the absorption of light. The indices found by Quincke by various methods are partly smaller than unity, partly very large; Wernicke finds for silver values between 3 and 5. On the other hand, Voigt calculates from Wernicke's observations the refractive index of silver at about 0.25.

Further, from observations on the reflexion of metals Beer‡ has deduced the velocity of light in metals according to Cauchy's theory, and Voigt† according to his own theory. On both theories the law of refraction of Snellius is certainly not

† Compare Voigt on the observations of Quincke and Wernicke, Wied. Ann. vol. xxiii. pp. 104-147, and vol. xxv. pp. 95-114.

† Pogg. Ann. vol. xcii. pp. 402-419.

<sup>\*</sup> Translated from the Sitzungsberichte der kön. Preuss. Akad. der Wissenschaften, Feb. 16, 1888.

true for metals. But the term "index of refraction" is to be used here also to denote the ratio of the velocity of light in vacuo to its velocity in the metal. The values calculated by Beer and Voigt agree in general. Both find the indices for gold and silver to be less than unity, for copper about equal to unity, and for the other metals values greater than unity.

A continued occupation with the optical properties of very thin metallic films induced me to investigate whether it would not be possible to prepare metallic prisms of very small angle and sufficiently transparent to permit of determining the prismatic deviation produced, and so arrive at a knowledge of

the velocity of light in the most direct way possible.

I have, in fact, succeeded in preparing such metallic prisms, and have determined for seven metals not only the mean refractive index, but for six of them the direction and approximate value of the dispersion. I believe that measurements with better optical instruments than those at my disposal, and with the necessary perseverance, might be carried out with much greater accuracy than I have yet attained. If, nevertheless, I conclude my experiments in the present preliminary stage, my excuse may be found in the fact that the work has already occupied two years, that the small number of usable prisms as recounted in the following pages had to be chosen out of more than 2000 made, and that, lastly, at least 2000 attempts were made before I learnt how to prepare the platinized glass upon which the prisms were electrolytically deposited in such perfection as was necessary for the purpose.

In the following pages I give, first of all, a short description of the method of preparing the prisms, then the method of observation and the results, together with a short discussion of them. Then follow some determinations of the index of refraction of metallic oxides; and, lastly, a comparison of my results with the values calculated by Beer and Voigt. conclusion, some observations to which my results naturally invite. It appears that the velocity of light in the metals stands in close relationship to their power of conducting electricity and heat; for in respect to the velocity of light the metals range themselves in the same order as in respect of their conductivity for electricity and heat. In order to establish a reliable and final relationship neither the extent nor the accuracy of my observations is sufficient. If, notwithstanding, I venture to draw wide-reaching conclusions from this general relationship, my object is chiefly to open the way

to further investigations.

## Preparation of the Prisms.

Most of the prisms were electrolytically deposited upon

platinized glass. At the commencement of my investigations I had two kinds of such glass at my disposal, viz. some pieces of French platinized glass taken from an apparatus made by König of Paris, and some pieces which Dr. Lohmann of Berlin had platinized for me. Only a very small portion of them possessed a sufficiently plane surface. Further, though the layer of platinum on these glasses is no doubt coherent, yet, as the microscope shows, it is far from uniform. latter circumstance is of no consequence when it is desired to deposit another metal in considerable thickness upon the platinum; but for the preparation of the prisms it is very prejudicial. As the stock of platinized glass was soon exhausted, and more was not to be obtained, either from Dr. Lohmann or from Paris, nothing remained but to prepare the platinized glass myself. After much trouble I succeeded in finding the composition of a platinizing solution which permitted the burning-in of the platinum at a low red heat, so that the plates remained perfectly even. Further, the film of metal was so perfectly uniform that even with high powers no want of homogeneity could be detected under the microscope. The plate-glass employed was about 6 millim. thick. The film of platinum was burnt-in in a small muffle-oven. It is unnecessary here to enter particularly into the details of the method, which will be described in another place. The metallic prisms were formed upon the platinized glass in the following manner:—Upon a strip of glass about 3 centim. broad, placed horizontally, a vertical electrode of the metal to be deposited, of equal breadth, was placed so that it did not touch the platinum. In the angle between the glass and metal a capillary layer of the electrolytic fluid was placed and decomposed by a current of suitable strength. A double wedge of metal was deposited whose greatest thickness lay directly against the metallic electrode. Whether the surfaces of the double wedge were in any degree plane, or whether they were strongly convex or concave, depended upon so many variable circumstances that the result was purely a matter of chance. Only those double wedges were of any use in which the surfaces were so far plane that they sharply reflected a fine wire cross when seen through a telescope provided with a Gauss's eyepiece. Often 50, and not unfrequently many more, prisms had to be made before one at all usable was obtained.

At first, when I used the thin (1.5 to 2 millim. thick) Paris and Berlin glass, they were, for the most part, not double prisms but single, which were obtained by plunging the metallic electrode vertically into the electrolytic bath, and bringing the platinized glass horizontally against it. There

is then deposited from the capillary layer of liquid, between the metal and the glass, a wedge of metal upon the glass and lying close to its edge. With silver the prisms were prepared, not only electrolytically, but by the chemical method of reduction. Prof. Quincke first showed how to obtain wedge-shaped films of silver from a solution of silver by placing the glass plate to be silvered upon a glass tube of suitable diameter. It was shown later that the films so obtained did not always increase steadily in thickness from the centre, but that the thickness increased periodically. From very many wedges prepared according to Quincke's method, it is, however, possible occasionally to find one in which the thickness increases continuously for a short distance, and where the boundary surface is nearly plane. The reflexion of a fine wire cross was again employed to test whether the surface was plane. Since, as is well known, no good deposit can be obtained with platinum electrolytically, it was necessary to find some other method. It is known that a platinum wire intensely heated by a current passed through it is disintegrated, and if a glass plate is brought near it the metallic dust is deposited upon it. In order to prepare prisms by this method a piece of platinum foil 0.015 millim. thick, 6 millim. wide, and about 45 millim. long, was stretched out, its sides vertical, directly above a glass plate placed horizontally. If the foil is then heated nearly to white heat, it becomes strongly disintegrated, and a double prism is formed upon the glass, which consists of a mixture of platinum and platinum oxide. intensely hot particles of platinum scattered from the foil appear, partially at least, to become oxydized by the atmosphere. The platinum oxide is easily converted into metallic platinum by gently heating. The double prisms, consisting of platinum and oxide, are therefore easily converted into pure platinum by heating.

Lastly, it was attempted to prepare double prisms of metal by volatilizing a metallic kathode in vacuo. A glass plate was brought as near as possible to, and parallel with, a metallic wire, which served as a kathode, and was intensely heated in vacuo by a powerful induction-current. As with the galvanically heated platinum coil, so here, a double wedge of disintegrated metal was formed. For the final experiments, related further on, such prisms are, however, not suitable. I give only in passing some of the numbers obtained with them.

## Methods of Observation and Results.

The indices of refraction are determined for the metallic prisms obtained in the manner described, assuming the truth of the law of refraction of Snellius, by measuring the angle

of the prism and the deflection.

The question whether the values thus obtained are really the reciprocals of the velocities of light in the metals is discussed further on.

If i denote the angle of incidence of a ray of light upon a transparent prism whose index of refraction is n, and for which the law of Snellius holds good,  $\delta$  the angle of the prism, and  $\alpha$  the angle of deflection which the emergent ray makes with its original direction, then

$$n = \frac{\sin (\alpha + \delta - i) + \cos \delta \sin i}{\sin \delta \sqrt{1 - \frac{\sin^2 i}{n^2}}}.$$

If  $\alpha$  and  $\delta$  are very small, as was always the case with the prisms used, and if, further, i is so small that  $\cos^2 i$  may be put equal to unity, then

 $n = \frac{\alpha + \delta}{\delta}$ .

With prisms of very small refracting angle, therefore, the deflection of the rays is independent of the angle of incidence

for small angles.

If, as in most of the following experiments, we have a double prism—of which, in consequence of the mode of preparation, both of the prisms have always nearly the same very small angle—the above formula, as is easily seen, holds if by  $\alpha$  and  $\delta$  we understand the sums of the deflections and of the refracting angles. The deflection is reckoned positive in the above formula if the pencil of light that has passed through the prism is deflected towards the thicker part of the prism, and consequently negative if the bending takes place towards the edge of the prism.

According to the formula given, it is not necessary to know the angles and deflections in absolute measure, e. g. in minutes and seconds; it is sufficient to determine them in any arbitrary measure. For these determinations a large Meyerstein's spectrometer was used. The instrument is provided with reading-microscopes; one division of the tangent-screw of these microscopes is equivalent to 1''·946. Since the angles to be measured are very small, it is not necessary to take readings upon the graduated arc itself, but the readings of the micrometer suffice. The values for  $\alpha$  and  $\delta$  are, therefore, given in the following Tables only in divisions of the micrometer—i. e. nearly in double seconds.

The glass plate supporting the small metallic prisms was

suitably cemented upon the plate of the spectrometer for the observations. An arrangement of screens was placed in front of it which, in the case of simple prisms, left free either the prism or a neighbouring portion of the glass, and in the case of double prisms the one prism and the other in succession. The angles of refraction, and in the case of double prisms the sum of the two angles, were determined in the usual manner by reflexion of cross-wires in a Gauss' eye-piece; the deflections by adjusting a fine cross of wires on the image of a slit. In both determinations the plate with the prisms remained fixed, and the divided circle with the observing telescope was turned. The side faces of the glass plate must be plane; but, as is easily seen, it is a matter of no consequence if

these faces have a slight inclination to each other.

According to the above formula it is sufficient to adjust the glass plate with the prisms at right angles to the incident rays by eye, although generally this adjustment was controlled by reflexion. Since the surfaces of the prisms are very small—2–3 millim. broad and about 10 millim. high—the pencil of rays received by the objective was very small; hence the adjustment of the eyepiece of the observing telescope in the right focal plane is more difficult, and the image of the slit, after passage through the thin prism, is never sharp, but has indistinct edges produced by reflexion. In order to avoid the dangerous errors resulting from insufficient adjustment of the observing telescope, observations by way of control were made each time, by the aid of which the telescope could be correctly adjusted. Into the details of this process it is not necessary to enter.

The deflection was always determined for white light—lamp, sun, or electric lamp. Notwithstanding that with some of the metals, as will be seen below, the dispersion is very large, yet with the small angle of the prisms used the deflection for white light could be determined exactly. The value observed applies to the mean rays of the spectrum. Then the deflection was determined for red and for blue light, for which purpose either the sun or the electric light was always

employed.

For observations in the red the rays passed through from one to four red glasses, according to the brightness of the source of light and the transparency of the prism; for the observations in the blue, through a blue glass, and a vessel with more or less concentrated solution of copper oxide in ammonia. Since it was not always possible to employ the same number of glasses and the same concentration of solution, the mean wave-length of the red and blue light used is not the same in all the experiments, so that the observations on dispersion are not strictly comparable amongst themselves

for all the prisms.

In most of the experiments, however, the maximum of the red light corresponds nearly to the line C, and that of the blue to the line G of the solar spectrum. The measurements of angle and deflection for the separate prisms, given in the following experiments, are in each case the mean of a large number of observations. In each case ten observations were made, and the mean taken as the value of the angle or deflection. For most of the prisms a number of such determinations was made; and the Tables give the final mean of all. The limits of error may be sufficiently seen from the differences which the several prisms show for n; it does not appear necessary to discuss the errors further. It may be remarked, however, that the main error results from the fact that the surfaces of the prisms were seldom perfectly plane. I have myself made all the adjustments; the readings of the microscope were made and noted by an assistant without reading out the several deflections.

I must not omit to express my thanks to the gentlemen who have assisted me in this work, Dr. L. Arons, Dr. C. Schmidt, and Dr. O. Wiener, the last of whom also assisted me in the manufacture of the prisms, and undertook certain measurements of angles made by way of control.

					Silv	er.		
No.	5.58 9.68 11.59 12.68 14.38 11.32 15.44 21.46	α.			n.			Remarks.
2.0.		Red.	White.	Blue.	Red.	White.	Blue.	2001141115
1 2 3 4 5 6 7 8			- 4·37 - 7·71 - 8·29 - 8·10 - 10·18 - 8·41 - 10·53 - 16·77	  Mean		0·22 0·20 0·28 0·36 0·29 0·26 0·32 0·22		Electrolytically deposited from a bath of silver potassium cyanide.  Chemically reduced.  The dispersion in silver is so small that it could not be measured.
					Go	ld.		
1 2	9·65 13·87	- 5·60 - 9·33		- 1·34 + 1·96	0·42 0·33	0.58	0·86 1·14	Electrolytically deposited.
Ī.				Mean	0.38	0.58	1.00	

## Table (continued).

	Copper.											
No.	δ.	α.				n.	*	Remarks.				
INO.	0.	Red.	White.	Blue.	Red.	White.	Blue.	hemarks.				
$\begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}$	8·55 12·31 11·75	- 4·70 - 6·74	- 3·05 - 4·23 - 4·10	+ 0.50 - 2.01	0·45 0·45	0.64 0.66 0.65	1.06 0.84	Electrolytically deposited from the Roseleur bath of copper potassium cyanide. A copper prism				
				Mean	0.45	0.65	0.95	from copper sulphate also gave strong normal dispersion, but the angle could not be accurately determined.				
Platinum.												
1 2 3	12·57 14·21 14·52	+ 9·50 + 9·23 +12·65	+ 8·27 + 8·50 + 9·61	+ 4.06 + 6.08 + 8.31 Mean	1.76 1.65 1.87	1.66 1.60 1.66 1.64	1·32 1·43 1·57	The prisms were obtained by disintegration of pla- tinum foil intensely heated in air by the elec- tric current, and subse-				
								quent reduction by heat- ing.				
					Iro	n.						
1 2 3 4 5 6	13.97 25.44 6.01 9.93 13.70 19.92	+10·21 +22·59 	$\begin{array}{r} + 9.66 \\ +17.83 \\ + 4.94 \\ + 6.29 \\ + 9.22 \\ +17.61 \end{array}$	+ 6·12 +15·13 	1·73 1·89	1.69 1.70 1.82 1.63 1.67 1.88	1·44 1·59	Electrolytically deposited according to Varrentrapp's method.				
				Mean	1.81	1.73	1.52					
					Nic	kel.						
1 2 3	9·12 9·56 9·50	+11.90 + 9.93	+ 9·16 + 8·09 +11·18	+ 8·26 + 7·41	2·30 2·04	2:00 1:85 2:18	1·91 1·78	Electrolytically deposited from nickel ammonium sulphate.				
				Mean	2.17	2.01	1.85					
					Bism	uth.						
1 2 3	12·87 14·20 23·79	+20·19 +21·56 +41·28	+15.31  +19.73  +28.71	+14·09 +17·96 +24·48	2·57 2·52 2·74	2·19 2·39 2·21	2·10 2·26 2·03	Electrolytically deposited from a tartaric acid bath of bismuth.				
				Mean	2.61	2.26	2.13					

## Discussion and Control-experiments.

I must refrain from discussing here at length all the possible sources of error of the methods of observation; I only mention some objections which might be made. It may be asked whether the refracting angle can be as correctly determined by observations on reflexion in our small and very thin prisms as with thicker prisms with larger faces.

It is known that if the thickness of a metallic film on glass increases continuously from zero, the change of phase upon reflexion at first changes with increasing thickness of metal, and only becomes constant after a certain thickness has been

attained\*.

If the prisms used were so thin near the edge that reflexion at different parts of the prism would be accompanied by different change of phase, then the whole plane wave reflected from the entire face of the prism might thus assume a direction differing from that required by the ordinary law of reflexion. In reply to this it is to be remarked that all the prisms used were so thick that the change of phase was the same at all parts. I have, however, employed two other methods of proving that the refracting angles were measured correctly. Dr. Wiener has, in fact, determined the angle of one of the

prisms used above by his method †.

The double prism of silver No. 5, which unfortunately was one of those with faces not perfectly plane, gave by observations on reflexion a sum of angles of a mean value of 14·38 divisions, corresponding to 27·98 seconds of arc. Dr. Wiener determined the sum of angles of the prism by his method at about 30". Converted into iodide of silver—the angle was determined by reflexion to be 67·59 divisions, or 131"·80. Wiener's measurement by the method of interference gave 128". The differences lie well within the limits of errors of observation. A film of silver increases upon conversion into iodide to about four times its thickness; consequently the angle of the silver-iodide prism must be four times that of the original silver prism.

From the value 67.59 divisions the angle of the silver was calculated to be 16.89, whereas 14.38 was observed directly. The difference is indeed somewhat large, but if it is remembered that this prism had faces not perfectly plane, the dif-

ference still lies within the limits of error.

\* Compare Wiener.

<sup>†</sup> Wied. Ann. Bd. xxxi. pp. 629-672.

The silver double prism No. 2 of the above Table gave for the sum of the angles of the prism in three observations the values:—

 $\begin{array}{c}
 8.45 \\
 10.26 \\
 10.32
 \end{array}$  Mean 9.68 divisions.

The same converted into iodide of silver gave the angles

 ${45.42 \atop 46.30}$  Mean 45.86,

which corresponds to an angle of 11.47 for the silver.

So also a bismuth prism and a nickel prism, converted into oxides, gave angles from which the angles of the metallic prisms could be calculated with a sufficient agreement with

the angles directly measured.

If the refracting angles are correctly measured by reflexion, the observations of deviation can hardly be falsified by variable change of phase. Nevertheless it might be supposed that the diffraction of light might influence the observations of deflection. The small aperture of the prism itself of course produces a marked diffraction; and even with the best prisms the image of the slit is not given with perfectly sharp edges. Moreover the absorption of light by the prism increases towards the base. I believe, therefore, that I have established, by numerous experiments, that refraction produces no constant error in the determinations of deflection.

Further, the circumstance that prisms of very different aperture, very different angles, and different thicknesses, in which, consequently, the decrease in the intensity of light at increasing distance from the edge of the prism was very different, gave values of a not affected by any regular change, shows that diffraction could introduce into the observation no

error which would be greater than the general errors.

Finally, we have the important question, What meaning is to be given to the values of n calculated from the observations? We see from the numbers given that n is a constant for each metal and a given kind of light in the neighbourhood of the angle of prism employed, and does not depend in any definite way on the value of these angles, which varied in the case of iron and silver from one to four. n is of course a magnitude characteristic of the optical behaviour of the metal. If n, as in the phenomena of transparent media, is the ratio of the velocity of light in the surrounding medium (in our experiments, air) to its velocity in the metal, then, if

the metal prisms are brought into another medium, the deflection of the rays would alter—in correspondence with the refractive index of the new medium. In order to try this, experiments of the following kind were made. Upon the glass plate carrying the prism a second glass plate was cemented at a short distance from it, and the space between was filled with a fluid, and the deflection was determined again. If  $\alpha'$  be the new deflection and n' the index of refraction of the fluid with reference to air, and if  $\alpha$  and  $\delta$  have the same meaning as before, then, remembering that the angle is small, we have

$$\alpha' = \delta(n - n'),$$

and

$$\alpha - \alpha' = \delta(n'-1).$$

We can thus calculate the deflection  $\alpha'$  from the value of n' determined in some other way, and from the difference between  $\alpha'$  and  $\alpha$  the value of n'.

The following small table contains the results of three experiments. White light was used; the value of n' being determined by means of a spectrometer for sodium light:—

Metal prisms in Fluid.

	Obs	Calcu	lated.						
δ.	α.	α'.	n'.	æ'.	n'.				
25.44	+17.83	Iron prism in oil of lavender, +17.83   +7.08   1.44    +8.64							
8:55	-3.05	-7.26	n in bone-   1.47	-7.01	1.49				
14.52			rism in wa   1 <sup>.</sup> 33		1.36				

The observed and calculated values agree very well together.

This appears to me to furnish the proof, so far as a purely experimental proof is possible, that the above calculated values of n really give the velocities of light in the metals.

Comparison of these Results with those calculated from the Indices of Refraction calculated by Beer and Voigt.

In the following table I have brought together the mean of the measurements given above:—

## Comparison of Mean Values of n.

	Red.	White.	Blue.
Silver Gold Copper Platinum Iron Nickel Bismuth	0·38 0·45 1·76 1·81 2·17 2·61	0·27 0·58 0·65 1·64 1·73 2·01 2·26	1·00 0·95 1·44 1·52 1·85 2·13

The velocity of light in silver is nearly four times as great as in vacuo, but the dispersion in silver is not very great. Also in gold and copper the velocity is greater than in vacuo but the dispersion normal; in all the other metals examined the dispersion is greatly abnormal. The values calculated by Beer and Voigt agree with these essentially, one may say in a surprising manner.

Beer has calculated the indices of refraction, *i.e.* the ratio of velocities in metal and *in vacuo* according to Cauchy's theory from Jamin's observations on reflexion. He finds for silver no marked dispersion and a mean refractive index 0.25. Copper gave strong normal dispersion, and for the red rays n < 1; iron gave anomalous dispersion,  $n_{\text{red}} = 2.54$ ,

 $n_{\text{violet}} = 1.47 *$ .

Voigt has elsewhere calculated the value of n according to his theory of the optical properties of the metals, from the observations upon reflexion made by Jamin, Haughton, and Quincke.

The values of n obtained for one and the same metal are somewhat different; the reason of this may be that the different observers have not used for their experiments metals of equal chemical purity and similar physical condition.

The values calculated are, however, less than unity for silver and gold and for the red rays in copper. So also Voigt finds normal dispersion for copper, but anomalous dispersion

<sup>\*</sup> Pogg. Ann. xcii. p. 417, 1854.

for iron, nickel, platinum, and bismuth. There is a considerable difference between the absolute value of n as calculated from my observations and from those of Voigt. This probably also arises from differences in the materials used.

Voigt has further shown, in a separate treatise\*, that according to his theory the refractive index of strongly absorbent media can be correctly determined in the ordinary way by prismatic deflection, if only the refracting angle of the prism is sufficiently small. The quantity  $\frac{n^2k^2}{2}\sin^2\delta$ , in

which n denotes the index of refraction, k the coefficient of absorption, and  $\delta$  the angle of the prism, may be neglected. This is always the case with our prisms; and thus, according to Voigt, also our assumption made above is justified that the values obtained for n are the reciprocals of the velocity of

light.

It is not possible to enter upon a discussion of the measurements made by Herr Dessau† of the dark rings seen in conical metallic layers, with the values of refractive index here found, since he was not able to measure the rings with normal incidence. I will only remark that the anomalous dispersion in platinum, iron, and nickel does not necessarily require an anomalous order of the rings in the red and blue, since, according to the above values for n in the metals named, the wave-lengths for red always remain greater than for blue.

## Indices of Refraction of Oxides.

In the course of this investigation opportunity occurred of determining the indices of refraction of some compounds of the metals—and in particular of the oxides—chiefly in order to check the method of observation in different ways. Since for many of the substances examined the index of refraction has not hitherto been determined, I give some of the numbers obtained. I add some determinations on metals which were impure by reason of the presence of oxides.

<sup>Wied. Ann. xxiv. pp. 144-156.
Wied. Ann. xxix. pp. 353-376.</sup> 

	Silver Iodide.										
No.	δ.		α.		n.			Remarks.			
		Red.	White.	Blue	Red.	White.	Blue.				
1 2 3	16.64 45.86 67.59	***	+21.71 $+53.07$ $+98.50$		•••	2:30 2:16 2:46		The prism was obtained by iodizing a silver prism.			
	Iron Oxide.										
1 2	12·09 25·71	+9:38	+13·41 +28·66	+16:40	1.78	2·11 2·12	2:36	The oxide prisms were obtained by heating the iron prisms to faint redness.			
	Nickel Oxide.										
1	24.27	+28.57	+29.88	+33.66	2.18	2.23	2:39	Obtained by heating a nickel prism to bright redness.			
				Bi	smuth	Oxid	e.				
1	20.82	•••	+18.94		***	1.91	•••	Obtained by heating a bismuth prism to redness. The dispersion was small, so that it could not be determined with certainty.			
	Copper Oxide.										
1	12.72	+20.75	+23.44	+27.71	2.63	2.84	3.18	Obtained by heating a cop- per prism to faint redness.			

## Platinum mixed with Platinum Oxide.

The prisms obtained by disintegration of platinum foil heated to redness by a galvanic current are a mixture of metallic platinum and oxides of platinum, which, as mentioned above, are only converted into pure platinum by heating. Since the composition is no doubt different in different prisms, there is little interest in determining the refraction of these mixtures. I give only a few values, as the indices are unusually large.

No.	δ.	δ.				n.			
		Red.	White.	Blue.	Red.	White.	Blue.		
1	40.56	+93.71	+93.02	+76.80	3.31	3.29	2.90		
2	12.35	+49.26	+47:23	+42.04	4.99	4.82	4.40		

The differences in the values of n in these two prisms far exceed the errors of observation; no doubt the percentage of oxide is greater in the second prism than in the first. It is worthy of remark that there is here a tolerably strong anomalous dispersion; but whether this depends upon the admixture of platinum or belongs to the platinum oxide cannot be determined.

The oxides of iron, nickel, copper, and bismuth show normal dispersion according to the above observations.

#### Gold with Gold Oxide.

I may remark that I had considerable trouble in preparing prisms of pure metallic gold. Those obtained by disintegration of a gold kathode almost all gave larger indices of refraction than those put down in the table on p. 7; this appears to result from the presence of traces of oxides of gold. So also with the prisms electrolytically deposited from solution of gold potassium cyanide, some of them gave larger indices of refraction.

It is possible that with the intensity of current employed small quantities of compounds of gold of different kinds might be deposited with the metallic gold.

The prisms which gave exceptional results were not green by transmitted light like those used above for measurement, but more or less violet, and occasionally even an intense reddish-violet. I give the following examples:—

No.	δ.		α.		n.			
		Red.	White.	Blue.	Red.	White.	Blue.	
1				Greenish   +2.47			d light.	
2	1			gration of $ +2.55 $			1.33	
3	Brigh	ht red, wi llic gold.	th small n	of a kath	tre. Con			

Connexion between the Indices of Refraction of the Metals and their Power of Conducting Light and Electricity.

If we glance at the values of n (compared on p. 12), the connexion between the indices of refraction and the conducting power of the metals for light and electricity at once strikes the eye. Those which have the smallest indices, and for which consequently the velocity of light is the greatest,

are also the best conductors of heat and electricity.

The galvanic specific conductivity and the coefficient of conduction for heat of a substance are perfectly definite values for a given temperature; the velocity of light in a body at a given temperature is not, for it varies with the wave-length. If therefore we wish to further investigate and formulate the above suggested universal connexion, we shall have to settle what is to be understood by the velocity of light. The formulæ of dispersion for transparent bodies lead always to a definite limiting value of index of refraction with increasing wave-length. That such a limit exists also for the metals cannot indeed be proved, but is probable. For our determinations those values are probably the nearest which were obtained for red light.

If we take the velocity of red light in silver as 100, then, according to the table on p. 12, we obtain the following

numbers for the other metals:-

Silver .					100
Gold .					71
Copper .				•	60
Platinum	•		•		15.3
Iron	•	•*			14.9
Nickel .	•		•		12.4
Bismuth					10.3

A glance at the above table shows that with one exception, viz. bismuth, the values of v fall within the limits of the numbers for the electric conductivity, obtained by the different observers, when that of silver is taken as  $100^*$ . The number 60 for copper appears somewhat too small. It is, however, to be observed that the electrolytic copper of our double prism might possibly contain some cuprous oxide, which would make the index of refraction too great, and the velocity of light too small. The conductivity of bismuth is given by all observers considerably less than 10. The bismuth with which the determinations of conductivity were made was, however, always

<sup>\*</sup> Wiedemann, Lehre von der Electricität, 3rd edit. vol. i. p. 503.

crystallized. The thin films of metal constituting the bismuth prisms, however, showed under the microscope no trace of crystalline structure; therefore the conductivity of the thin uncrystallized film of bismuth used might very well be a quite different one, and better than that of a crystallized rod. ratio of the conductivities for heat and electricity has also been

found to be very different by different observers.

We may therefore, on the basis of the above numbers, come to the conclusion that the electric conductivity in metals is really proportional to the velocity of propagation of lightwaves of long period. In order to test this supposition, it would be necessary to determine the index of refraction of very long waves and the specific conductivity for the same piece of metal, or at least for metal electrolytically deposited in the same way. Whether such determinations could be carried out at all accurately must remain for future discussion.

If we conclude that the above proportionality has been proved, at least approximately, by our experiments, there must exist a very intimate connexion between the velocity of light and the conductivity for heat in the metals; for however great the differences between individual observations may be, it at least follows, from a comparison of the whole of the determinations at our disposal, that the conducting powers for electricity and heat in the metals are proportional to one another.

There thus exists at least a near proportionality between the velocity of light, electric conductivity, and coefficient of conduction of heat in the metals. This remarkable relationship indicates a connexion between the motion of light in the metals, the motion of electricity in the galvanic current, and of heat in a current of heat.

I have endeavoured to find an explanation of this by the assumption that the conduction of heat in a metal depends essentially upon radiation from one layer to the neighbouring one, in which the radiation takes place with the velocity of light in the metal in question; and that, on the other hand, what we call electricity moves in a metallic conductor traversed by a galvanic current with the velocity which light has in the metal. How far this view is tenable must be decided by more extended experiments than I have as yet been able to carry out.

In conclusion I would further remark that, if the approximate proportionality shown in our experiments between velocity of light and galvanic conductivity really exists, certain consequences would follow which are capable of being tested by experiment. I will only here mention two of them.

The conductivity of metals decreases with rising temperature; consequently the velocity of light must also decrease with rising temperature, and the index of refraction must increase. It is true that Sissingh was not able to observe a change in the reflexion-constant of iron with change of temperature\*, but the experiments cannot be considered decisive; the indices of refraction must be determined directly by measuring the prismatic deviation at different temperatures. I do not consider the experimental difficulties of such an investigation to be insurmountable. It is known also that the electric resistance of metals varies differently in a magnetic field. Hence the index of refraction of a metal should be affected by magnetization. Should this change prove too small to be measured, yet under suitable conditions the æolotropism, which the metals suffer upon magnetization in respect of their conductivity, might be rendered evident by optical means by the double refraction of light produced.

II. A Theory concerning the Sudden Loss of the Magnetic Properties of Iron and Nickel at certain Temperatures. By Herbert Tomlinson, B.A.†

THAT very high temperatures destroy both the magnetic susceptibility of iron and its power of retaining magnetism has been known since the days of Queen Elizabeth. Thus Gilbert found that a loadstone and a piece of iron equally lost their power of affecting the magnetic needle when very hot; he also noticed that whilst the magnetic property returned to the iron after it had cooled a little, the magnetic virtue of the loadstone was altogether destroyed. Similar results were obtained by Brugmans, Boyle, Cavallo, Barlow and Bonnycastle, Christie, Ritchie, Erman, Scoresby, Seebeck, and others ‡. Faraday found that a steel magnet lost its permanent magnetism rather suddenly at a temperature a little under the boiling-point of almond oil (the best bitteralmond oil boils at 180° C.); it behaved like soft iron till it was raised to an orange-red heat, and then lost its magnetic susceptibility and became indifferent. The temperature at which the retentive power for permanent magnetism was lost appeared to vary in steel with the hardness and structure; in fragments of loadstone it was very high; they retained their

<sup>\*</sup> Sissingh, "Mesures de la polarisation elliptique de la lumière," Archives Néerlandaises, t. xx.

<sup>†</sup> Communicated by the Physical Society: read April 28, 1888. ‡ See Professor Chrystal's Article on Magnetism, Enc. Brit.

permanent magnetism until just below visible ignition in the dark (this would be somewhere about 500° C.), but lost their susceptibility at a much lower temperature than the steel. Nickel was found to lose its susceptibility about 330° C. to 340° C. (according to Becquerel about 400° C.; according to Pouillet 350° C.). Gore has published accounts of experiments relating to the sudden loss of magnetic properties of both iron and nickel at certain temperatures\*. Chrystal†, in the course of some experiments on the magnetic sounds in iron, nickel, and cobalt when traversed by an interrupted current of electricity, found evidence of sudden changes in the magnetic susceptibility of iron and nickel at certain temperatures, and gives some curves which enable us to trace the connexion between these changes and the equally curious changes of thermoelectrical power observed by Tait in iron and nickel at certain temperatures ‡. Baur § and Wassmuth | have also taken up the matter. According to the former, for small magnetizing forces the susceptibility of iron at first increases rapidly as the temperature increases, reaches a maximum at red-heat, and then falls suddenly to zero. For large forces the susceptibility decreases gradually up to red-heat, and then falls suddenly to a very small value. According to him, if a bar be cooled from a white heat the first traces of susceptibility are observed at a very bright red, the brighter the greater the magnetizing force. Berson I has published a curve showing the relation between the magnetic induction of nickel and the temperature right up to the point at which the susceptibility practically vanishes, namely, 336° C. The author\*\* has also quite recently published similar curves for nickel, and finds that the susceptibility practically vanishes at temperatures ranging from 333° C. to 412° C. according to the strength of the magnetizing force, the greater the force the higher the temperature. The author, like Berson, finds the temperature at which the nickel begins to rapidly lose its temporary susceptibility to be 300° C. Ledeboer †† has published similar curves for iron. He makes the susceptibility of iron to vanish

<sup>\*</sup> Proc. R. Soc. vol. xvii. p. 261 (1868-1869); Phil Mag. vol. xxxviii. p. 60 (1869); Phil. Mag. vol. xl. p. 175 (1870). For extracts see Electrician, vol. xx. Nos. 505, 506. + 'Nature, vol. xxii. (1880).

<sup>†</sup> Heat, pp. 176–178; Trans. R.S.E. (1873). § Wied. Ann. xi. (1880). || Wien. Ber. (1880, 1881, 1882).

<sup>¶</sup> Ann. de Phys. et de Chim. vol. vii. (1886). \*\* Phil. Mag. vol. xxv. No. 156 (1888).

<sup>††</sup> La Lumière Electrique, tome xxvii. no. 2.

at temperatures ranging from 750°C. to 770°C., the higher the greater the magnetizing force. The temperature at which the iron begins to suddenly lose its temporary magnetic

susceptibility is about 680° C.

The author\*, in a paper on the recalescence of iron, was led by his experiments to express a strong conviction that with iron there are two critical temperatures at which profound changes take place in the molecular architecture of the metal and at which heat becomes latent. The lower of these critical temperatures he fixes at 550° C. and the higher at 1000° C. Previously to this, but unknown to the author, Pionchon†, by most carefully conducted calorimetric researches, had also found in iron two critical temperatures at which heat becomes latent, namely, 660°C.-720°C. and 1000° C.-1050° C. He fixes the value of the latent heat at the lower temperature at 5.3 (about 15th of the latent heat of ice), and that at the higher temperature at 6.0. Pionchon also expresses the specific heat of iron by the following formulæ, in which y is the specific heat at the temperature t° C.

0° C. to 660° C.  $\gamma = 0.11012 + 0.00005066t + 0.000000164t^2$ . 660° to 720°  $\gamma = 0.57803 - 0.002872 t + 0.000003585 t^2$ . 720° to 1000°  $\gamma = 0.218$  $1050^{\circ}$  to  $1200^{\circ}$   $\gamma = 0.19887$ .

The author now believes that the lower of the two critical temperatures quoted by him previously, and deduced from his own experiments on the internal friction of iron, may be a third critical temperature, and not, as he at first supposed, the temperature at which iron begins to suddenly lose its magnetic properties, which last seems beyond a doubt to be Pionchon's first critical temperature.

In the researches of Moissan § on the allotropic modifications of iron oxide two temperatures are very conspicuous,

namely, 700° C. and 1000° C.

The following table, compiled from the various researches mentioned above, will show at a glance the different critical temperatures of nickel and iron which the author believes may exist :-

\* Phil. Mag. Feb. 1888.

<sup>†</sup> Ann. de Phys. et de Chim. t. xi. (1887). ‡ If this be so, there is probably another sudden change in the internal friction at 680° C.

Ann. de Phys. et de Chim. t. xxi.

<sup>|</sup> The changes taking place at A may, however, be due to approach of the critical temperature B.

#### Nickel.

A. 

200° C. Specific heat of electricity changes sign.
200°. For low magnetizing forces the magnetic susceptibility begins to rapidly increase.

B. 
 {300°. Magnetic susceptibility begins to very rapidly decrease.
 320°. Specific heat of electricity again changes sign.

#### Iron.

A. \begin{cases} 550\circ C. Specific heat of electricity changes sign. 550\circ Internal friction of iron begins to rapidly increase.

B. \$\begin{cases} 680^\circ\$. Specific heat of electricity again changes sign. \\
680^\circ\$. Magnetic susceptibility begins to very rapidly \\
decrease. \\
660^\circ\$-720^\circ\$. Heat becomes latent.

1000°. Very rapid increase of internal friction.

C. 

1000°. Very rapid increase of internal friction.
1000°-1050°. Heat becomes latent.
About 1000°\*. Remarkably sudden permanent yielding when under stress, and equally remarkable temporary changes when under stress or strain. Also at this temperature hot iron, which at any temperature is thermoelectrically negative to cold iron, becomes suddenly much more negative.

In the above table the author has not included certain remarkable changes which take place in the electrical conductivity of nickel and iron †, because these do not appear to be sufficiently near any of the above critical points. Thus Smith and MacGregor make the electrical conductivity of pure nickel foil to change suddenly at 149°C., a temperature considerably below 200° C.

Neither has the author included certain remarkable changes which have been observed to occur in the thermal expansion of steel at high temperatures ‡, because in the first place there are no such remarkable changes in iron §, and in the second the critical temperature in the thermal expansion of steel varies very considerably with different specimens; thus in three specimens we have abrupt changes at the temperatures

\* At least as judged by the colour.

† Macfarlane, Proc. R. S. E. 1875; C. M. Smith and J. G. MacGregor, Proc. R. S. E. 1875, 1876.

† Nouel, Génie civil, April 1887.

In the curve showing the relation between the thermal expansion of iron and the temperature there is a very slight inflection at 400° C.

660° C., 680° C., and 725° C. The author has himself examined the thermal expansion of *iron* at different temperatures right up to and a little beyond that at which the metal showed very conspicuously sudden loss of magnetic properties without at the same time detecting anything like a sudden change in its thermal expansibility.

Evidently the critical points A and B, though occurring at a much lower temperature in nickel than in iron, correspond to similar molecular changes in the two metals, but the third critical point C in iron has apparently no corresponding point in nickel. There are at any rate no such sudden changes in

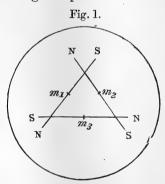
nickel when under stress and strain as occur in iron.

It is, however, the critical point B in nickel and in iron which concerns the present inquiry. Why does the temporary magnetic susceptibility of both these metals diminish so rapidly that, if an iron or nickel wire be surrounded by a magnetizing solenoid always kept in action, and this again be concentric with a secondary solenoid connected with a galvanometer, a very sensible induced current can be observed at the critical temperature both on heating and cooling\*? This question is a very important one, and if we can answer it correctly much light will doubtless be thrown upon the nature of magnetism.

According to the author's view of the matter each molecule of iron, say, contains within itself several magnetic molecules

(it may contain several hundreds or thousands).

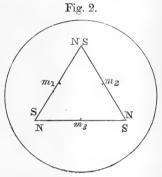
Let the circle in fig. 1 represent a molecule of iron, and



let  $m_1$ ,  $m_2$ , and  $m_3$  be the centres of the axes of three magnetic molecules. Each of these magnetic molecules, like

<sup>\*</sup> Even when the wire is only under the influence of the vertical component of the earth's magnetic force, the currents induced when the magnetic properties are lost or restored are quite sensible.

the molecule of iron itself, is capable of motion of rotation and of motion of translation. At ordinary temperatures the magnetic molecules have their centres  $m_1$ ,  $m_2$ ,  $m_3$  so close together that though they are endeavouring to form a closed magnetic circuit they are unable to do so. If now we apply a magnetizing force in any direction, each magnetic molecule will be rotated about its axis, and the whole iron molecule will be magnetized and rotated about its axis. When the magnetizing force is removed both the magnetic molecules and the iron molecules will return more or less completely to their original positions. On raising the temperature the centres of both the iron molecules and the magnetic molecules will increase their distances from each other until a certain temperature is reached. when the opposite poles of adjacent magnetic molecules will come into such close proximity that they will be able to rush together so that the system of magnetic molecules forms a close magnetic circuit, as in fig. 2. When the magnetic



molecules are in this position a small magnetizing force in any direction will have no appreciable effect; but by employing larger and larger magnetizing force we may obtain sensible evidence of magnetization, as indeed Faraday, Baur, and the author have found. The suddenness of the loss of magnetic properties is easily comprehended when we remember the rapidity with which magnetic attractions increase as the distance between magnetic poles diminishes. We can also understand that heat at this point should become latent, for it is evident that the sudden bringing together of N and S poles, which takes place on heating, will cause a sudden expansion of  $m_1$ ,  $m_2$ , and  $m_3$ . Since the action goes on inside the iron molecule there may be no sensible sudden increase of distance between the centre of one iron molecule and another, and no sensible change in the molar dimensions of the iron. This agrees with the fact ascertained by

M. Nouel and the author that, at any rate in the case of annealed iron, there is no sudden change in the thermal expansibility at this critical temperature.

When the temperature, after it has been raised to the critical point, is again lowered, the centres  $m_1$ ,  $m_2$ ,  $m_3$ , will creep closer together again and the magnetic properties will

reappear as suddenly\* as they were lost.

According to the theory, it would seem that if we could make the magnetic molecules assume a sufficiently closed magnetic circuit, iron and nickel might be converted into diamagnetics. Indeed we can understand that diamagnetics may be such in consequence either of a paucity of magnetic molecules in each molecule of the substance, or from having their magnetic

molecules forming nearly closed circuits.

Again, if the temperature be raised high enough it would seem possible to partly restore the lost magnetic susceptibility; for then, by the further expansion of  $m_1$ ,  $m_2$ , and  $m_3$ , the N and S poles would begin to be separated. If, therefore, such metals as bismuth are diamagnetic at ordinary temperatures, partly because their magnetic molecules form closed circuits, rise of temperature should make them more magnetic or less diamagnetic. This seems to be the case, for the experiments of Plücker and Matteucci led them to conclude that the susceptibility of diamagnetics diminishes with increase of temperature; in the case of bismuth the decrease between ordinary temperatures and its melting-point is said to be about one sixth or more †.

The following experiments were made with the apparatus which has already been described ‡. The wire to be examined was suspended vertically in the axis of a glass tube, being clamped at its upper extremity into a brass block resting on a wooden support fitting on to the top of the tube, and provided with a terminal screw for making connexion with one pole of a battery of thirty Grove's cells. The current from this battery was employed to heat the wire and passed in or out of the latter through the intermediation of a mercury-cup, into which dipped a stout copper wire attached to a brass block clamped to the lower extremity of the wire.

### Experiment I.

A piece of very soft and well-annealed iron wire, 30 cm. long and 1 mm. in diameter, was suspended in the glass

† Chrystal, Enc. Brit., Art. Magnetism. † Phil. Mag. vol. xxiv. p. 258,

 $<sup>\ ^*</sup>$  The suddenness of both loss and gain of magnetic susceptibility may also be conditioned by internal friction.

tube, so that it could freely swing torsionally. The glass tube was placed inside a magnetizing solenoid, which was in turn coaxial with a secondary solenoid connected with a Thomson's reflecting-galvanometer. The magnetizing solenoid was actuated by 2 Grove's cells, which were kept in action throughout the experiment. As soon as the current from the 30 Grove's cells had heated the wire to a dull red, there was a slight deflection of the Thomson's galvanometer, indicating that the iron had suddenly lost part of its magnetic susceptibility; then, after a pause of three or four seconds, there was a much greater deflection of the galvanometer in the same direction. Again, when the wire was allowed to cool, there was first a slight deflection of the galvanometer, indicating partial restoration of magnetic susceptibility followed immediately by a much larger deflection\*. It seems likely that the interval between one deflection and the next, when the wire is being heated or is cooling, is the first of the two periods during which, according to Pionchon, heat is becoming latent. There is a similar pause, though not quite so marked, in the sudden jerk which occurs in an iron wire which has been permanently strained when the critical temperature C has been reached t, and when, according to Pionchon, heat a second time becomes latent.

## Experiment II.

In this experiment an attempt was made to abolish the deflections of the Thomson's galvanometer, due to the sudden loss or restoration of the magnetic susceptibility, by torsionally oscillating the wire during the whole period of heating or cooling. But no amount of torsional oscillation availed anything.

## Experiment III.

The experiments of Faraday and others, quoted previously, show that there is a temperature at which permanent magnetization in steel begins to be rather suddenly lost, and that this temperature is considerably lower than the temperature at which the temporary magnetic susceptibility begins to rapidly diminish. The author has also found that when a permanently twisted wire is heated it begins at a certain temperature to rapidly ‡ lose its permanent strain. It seemed,

<sup>\*</sup> This pause between one deflection and another has already been noticed by Mr. Newall (Phil. Mag. vol. xxiv. p. 435).

<sup>†</sup> Phil. Mag. vol. xxiv., 1887.

<sup>†</sup> This sudden loss of permanent strain must not be confounded with the sudden jerk which takes place at the critical temperature C.

therefore, desirable to ascertain if this sudden loss of permanent molecular strain would, like permanent magnetization. take place at a lower temperature than the loss of temporary susceptibility. The iron wire in the last experiment was. therefore, permanently twisted through twenty revolutions and then released from torsional stress. When, on heating, a certain temperature had been reached there was a sudden untwisting of the wire, followed after an interval of several seconds by the usual deflection of the Thomson's galvanometer, which showed that the temporary magnetic susceptibility was This experiment was repeated at beginning to disappear. least six times with different pieces of the same kind of wire. and, invariably, with the same result—the permanent torsion, like the permanent magnetism, began to disappear suddenly at a temperature considerably below the temperature at which the temporary magnetic susceptibility began to disappear.

The contrary, however, was the case with a specimen of annealed nickel wire\* of the same length as the iron but of rather less diameter. When this wire had received a few turns of permanent torsion†, and was afterwards heated, the loss of temporary magnetic susceptibility occurred at a much lower temperature than the rapid loss of permanent torsion; whilst Berson has shown that the permanent magnetization of nickel resembles the permanent magnetization of iron in

disappearing before the temporary susceptibility.

This experiment, therefore, shows that the temperature at which permanent magnetism begins to suddenly disappear is not the temperature at which permanent torsion begins to suddenly disappear.

III. On a Diffusion Photometer. By J. Joly, M.A.B.E.‡

A PECULIAR appearance presented by a translucent substance, when rendered discontinuous by a crack or break, is probably a matter of common observation. When such an object—it may be the familiar one of a cracked paraffin candle—is placed in an unequally illuminated field, the presence of the discontinuity shows out, in general, boldly, as a plane of separation between a bright and a dark portion of the substance. The light, in fact, diffused through the substance, passes only in a feeble degree across the crack, so that that part of the body near the source of light appears

\* Containing nearly 98 per cent. of nickel

<sup>†</sup> Only two or three turns can be given before the wire breaks. ‡ Communicated by the Author.

filled with diffused light, that part furthest removed dark and obscured. The crack may be very minute, the effect is the same. Only when the edge of the crack is so turned that the source of light shines equally on either side of it, or if two sources of light of similar colour illuminate separately and with equal intensities the material at either side of the crack, does the discontinuous appearance vanish. On this effect the

photometer to be described is based.

If, in fact, two parallelepipeds of paraffin be cut, of equal dimensions, and planed smooth so that they can be laid accurately together on similar faces, it will be found that a very sensitive apparatus is obtained, so that an appearance of homogeneity is only secured by nice adjustment to a plane of equal illumination. To compare two sources of light it is sufficient to place the compound parallelepiped with its plane of discontinuity at right angles to the line joining the sources of light and cut by this line. Then, shifting the parallelepiped between the lights, and regarding the fine line of division on its surface, to find the point at which this line is no longer, or only with difficulty, descernible. The distances are now measured in the usual way, and the relative intensities of the light reckoned as inversely as the squares of their distances from the plane of juncture of the parallelepiped.

In the case, however, of lights of dissimilar colour, the appearance of the photometer is no longer uniform, but that of two softly glowing substances having different shades of colour. The difficulty now of judging when equilibrium is obtained is one which must arise with all photometers which are true to colour. So far, however, as my experience goes, comparing the gas-flame with the candle, the comparison of intensity is not possessed of any uncertainty, the line showing with a minimum of distinctness when the brightness at each side is the same, and the position of equilibrium being reformed with great accuracy on repeated observation. In extreme cases tinted glasses interposed in front of the flame might be used.

The explanation of the sensitiveness of this photometer is not far to seek. The surfaces being compared are in juxtaposition and simultaneously in the field of vision. If, now, we concentrate all our attention close to the line of junction, the least disturbance in the equality of the illumination will be most favourably displayed to the perception. The light entering the eye, too, is soft and perfectly uniform over the surfaces regarded. Photometers in which a kind of visual memory has to be exerted in the comparison of two images removed some 8 or 10 centimetres from one another do not possess the same sensibility. There is, also, a notable absence

of the fatigue attending the use of apparatus which constrain us to shift our attention from one image to another.

Recently I have changed the nature of the material to the more durable one of glass, of very similar translucency. It may be said that the nearer the glass approaches the uniform soft translucency of paraffin the better it is for the purpose. The durability secured in the use of this material and the accuracy of surface it permits in grinding and polishing are great advantages. I have also heightened the effect of the plane of separation by interposing between the parallelepipeds a film of silver leaf. This is caused to adhere by means of canada balsam, by which too they are finally cemented Thus prepared, their behaviour to light is very striking. In a plane of luminous equilibrium they appear as a single body lit up internally and emitting a soft light. The least flicker in one of the sources of light destroys the illusion of uniformity, and a screen interposed at one side seemingly reduces the parallelepiped to half its size.

The dimensions I find most suitable are  $20 \times 50 \times 11$  mm. for each parallelepiped. They are laid together on two of the larger faces, the parallel external faces being ground smooth, but left unpolished. The surface under observation during experiment is ground smooth and polished after the joining of the parallelepipeds. The most important points to be attended to in their construction are fineness of divisional line and uniformity in thickness. Should there be any difference in the translucency of the parallelepipeds a check observation might be made by turning over the photometer so that the halves change places relatively to the lights, taking a mean of the results. This has not been necessary with such prisms as have come under my notice.

In judging of the final position of equilibrium I am accustomed to magnify the line with a lens, but I find many observers prefer the absence of the lens. To shelter the photometer from disturbing effects of reflexions, &c., I use a blackened box, somewhat similar in form to that used with the Bunsen photometer, but smaller in size. The usual precaution of protecting the eyes of the observer from the direct rays of the lights should, of course, be observed.

The effect upon which this photometer is based will be extensively observed in natural objects, as translucent minerals, where any discontinuity of substance, as a cleavage crack, occurs.

A note on the above appeared in the Proc. Roy. Dublin Soc. (vol. iv. p. 345, Dec. 1884), and the photometer was exhibited before the Berlin Physical Society by Dr. König ('Nature,' xxxiv. p. 48).

IV. On a Method of Determining the Specific Gravity of Small Quantities of Dense or Porous Bodies. By J. Joly, M.A.B.E., Trinity College, Dublin\*.

IT may happen to be of importance to the mineralogist or to the chemist to determine the specific gravity of a very minute quantity of a solid. A method of effecting this, whatever the density of the solid or whatever its state of aggregation, is described in the following note. It, moreover, calls for the use of no special appliance. The method now in general use for the micro-determination of the specific gravities of silicates, &c., of low density, is by balancing in a liquid of a specific gravity adjustable to that of the specimen, and subsequently determining the density of the solution employed.

This method fails altogether,

(1) when the substance has a specific gravity over four;

(2) when the substance is of a porous nature.

In the first case the method fails for want of a liquid of sufficient density to equilibrate the solid. Be it observed that about 90 per cent. of the unsilicated mineral species range

in density above 4.5.

In the second case—the case of porous bodies—the impossibility of freeing the body entirely from contained air, when immersed in liquids of the nature of those to which we are restricted, renders the method fallacious. There is another source of error. The particle in the first instance soaks in a certain quantity of liquid at such a density, subsequently the density of the liquid surrounding it is brought to another density. Is it assured that the density of the liquid lodged in the interstices of the substance in the first instance assumes the density subsequently conferred on the surrounding liquid? It might need a considerable time for the desired equalization of density to occur.

Briefly, the theory of the present method is as follows:—
The mineral by itself will not float in any known solution, suppose. If, however, we mix it with another substance of much lower specific gravity, there is easily found such a proportion for the constituents as will enable the mixed bodies to be equilibrated by dilution of the specific gravity liquid. We may, in short, adjust the specific gravity of the mixed substances to be as close to that of either of them as we

please.

We require to know—

<sup>\*</sup> Communicated by the Author.

W the weight of the mineral, ω ", ", ", buoyant substance,
σ ", sp. gr. ", buoyant substance,
s ", " mixed substances,
in order to determine S, the specific gravity required.

Then, as

sp. gr. =  $\frac{\text{weight}}{\text{volume}}$ ,  $S = \frac{W}{\frac{W + \omega}{s} - \frac{\omega}{\sigma}},$ or  $S = \frac{W\sigma s}{(W + \omega)\sigma - \omega s}.$ 

By this means, then, we can deal with bodies of any specific gravity; and, further, if for the buoyant substance we chose one which, when brought to the liquid state, will creep into and surround the substance, we may evidently be independent of conditions of aggregation, and all trouble with contained air, or bubbles adhering to the surface of a rough fragment, avoided.

The method is practically carried out in the following

manner :-

The specific gravity of a piece of translucent, homogeneous paraffin, free from bubbles, is taken by any of the ordinary methods—weighing in water with a sinker, or balancing in a mixture of alcohol and water, and then determining the density of the solution. The value found is what is called  $\sigma$ above, the specific gravity of the buoyant substance. There is no better paraffin for our purpose than that sold in the form

of candles. It fulfils all requirements.

From this piece of paraffin a little disk-shaped piece—about 3 or 4 mm. in diameter, and 1.5 mm. thick—is cut with a sharp knife, cleanly paired and smoothed on the edges by gently rubbing between the fingers. The disk is larger or smaller according to the quantity of mineral at our disposal, and if great accuracy be desired we determine its specific gravity, thus avoiding any assumption as to the homogeneousness of the piece from which it is cut. There will be in general, however, no need for so doing: thus, compare the two following specific gravities obtained—(1) on a piece of paraffin weighing over 11 grms.; (2) on a little disk removed from this, and weighing about 04 gram. (2) was determined by balancing in dilute alcohol:—

> (1) 0.9204(2) 0.9208

—an inappreciable difference of specific gravity. The large piece may be preserved for future determinations.

The disk removed is next weighed in a delicate balance. as small as described above, the balance should read definitely to 0.2 mgr. Its weight is w in the equation. It is in all cases manipulated by use of a clean ivory forceps. If very minute it is weighed on a tared watch-glass, and so need not be manipulated at all after preparation. Removed from the balance, the small fragment (or fragments) of mineral is placed upon the surface of the disk. The extremity of a slip of copper, about 5 mm. wide, is now heated in a smokeless flame—it is better to use a little copper ball, drilled and fitted on to a fine steel knitting-needle—and held above the fragment of mineral, care being taken not to approach it so closely as to endanger the paraffin being volatilized or of its being melted so far as to risk loss by running over. Preferably the disk of paraffin should rest on a piece of clean copper; this will keep the lower surface cool. In point of fact, the mineral in general absorbing heat more freely than the paraffin, melts the paraffin beneath it by conductivity, and there is little The heating is continued till the mineral is risk of loss. seen to be completely soaked with the paraffin—every crack and cranny is then filled, the paraffin welling up and swallowing the specimen and expelling all trace of air.

When cold it is placed in the balance and weighed. By subtracting  $\omega$  from the weight found, we have W, the weight

of the mineral.

There is probably no loss of paraffin in this process. Thus it will be found that if such a pellet be very carefully balanced in a solution, removed, dried, and melted on the hitherto unaltered face of the disk, and then replaced in the solution, there is, if anything, a slight decrease of density; on complete

cooling this decrease is inappreciable.

The pellet is now dropped into a specific gravity solution. A saturated solution of common salt and water (sp. gr. about 1.2) will in many cases be found sufficient to float it. If so, we have merely to adjust by adding water. Otherwise we resort to Thoulet's solution (Minéralogie Micrographique, Fouqué et Lévy, p. 118). I have prepared no pellets approaching this density (2.77), but I prefer the use of this solution in all cases; it seems to concentrate less rapidly by evaporation, and is more "creepy."

In this operation of balancing it is advisable to use a camel's-hair brush for stirring, and also for conveying small quantities of liquid when finally adjusting—a process of much delicacy. The brush is also used for removing bubbles from the pellet, which, however, will be found to give little trouble if the solutions be previously boiled to expel air.

If the mixed solutions containing the pellet be left standing for some hours before finally adjusting, it will be found on examination with a lens that bubbles will no longer gather on the paraffin.

The last operation is finding the specific gravity of this solution, which gives us s in the formula. This is most accurately done in a Sprengel tube, holding about 2 cc.;

the bottle may also be used.

The table opposite contains the results of some determina-

tions made by the method.

Of experiments 4 and 5 it is interesting, perhaps, to note that 4 was undertaken with the notion that the mineral being dealt with was barite. Its weight, as a hand specimen, was deceptive, it being penetrated by sphalerite. On getting the result (2.78) it was concluded that an oversight had been made somewhere in the measurements, and experiment 5 was undertaken; this giving 2.77, the specimen was appealed to. Tests then showed it to be calcite. The determinations numbered 11 and 12 were effected on minute, greenish crystals, hexagonal in shape, removed from the Wicklow granite. The crystals alone sank rapidly in Thoulet's solution (sp. gr. 2.77). The foregoing method was resorted to, and the specific gravity of apatite being obtained, the substance was tested in the usual way. The tests being confirmatory, it was concluded that the mineral was apatite, a rare substance in this granite.

I have thought well to include in the table some of the quantities obtained in working the formula, as bearing on the scale on which the experiments have been made. It is evident that the method can be applied on a smaller scale still; weighing to tenths of milligrams, 10 milligrams could be dealt with. The method, it is seen, involves two weighings and one determination of specific gravity by balancing in a solution; that is, if a piece of paraffin of known specific

gravity be at hand.

Recently it has come to my notice that a method based on a similar principle is described in Rosenbusch's Mikroskopische Physiographie der Mineralien und Gesteine. In detail, however, the methods differ essentially. Thus in Rosenbusch's method the mineral is caused to adhere to a piece of wax by pressure, and is subsequently taken off and weighed after their joint specific gravity is determined. Here the difficulty of freeing the substance from contained or adhering air remains. A porous substance cannot be dealt with. They differ, too, in other respects, so that I am induced to think the foregoing may still, independently, be of use.

(Sp. gr. of Paraffin 0.9204.)

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				(~F	(Sp. 8. or + manner o 2011)		(TEC	
		Specific Gravity found.	Specific Gravity (Dana).	Weight of Mineral.	Volume of Mineral.	Weight of Paraffn.	Specific Gravity of Pellet.	Observations.
				Grammes.	Cub. Cms.	Grammes.		
1.	Orthoclase	2.63	2.5-2.6	0.0162	0.00615	0.0674	1.0545	(Co. Dublin.) Very loose and cleavable.
.2	Orthoclase	2.66	2.5-2.6	0.0237	0.00879	0.0562	1.1434	(Belleck.) Very loose and cleavable.
ల	Magnetite	4.81	4.9-5.2	0.0202	0.00419	0.0654	1.1361	(Krakatoa Ash.) Separated by magnet;
<u>4</u>	Calcite	2.78	2.5-3.5	0.0153	0.00547	0.0351	1.1557	(Co. Wicklow.) Foliated.
57	Calcite	2.77	2.5-3.5	0.0201	0.00726	0.0517	1.3967	From same specimen as 4.
6.	Tourmaline	2.98	2.9-3.3	0.0128	0.00429	0.0443	1.0973	(Glencullen, Co. Dublin.) Black.
.7	Gold	17.42	15.6-19.5	0.0352	0.00202	0.0322	1.8216	(Peru.) Mossy.
00	Galena	7.21	7.25-7.7	0.0283	0.00392	0.0441	1.3967	Well crystallized.
9.	Galena	7.18	7.25-7.7	0.0242	0.00337	0.0258	1.5921	From same specimen as 8.
10.	Cuprite	5.81	5.81-6.15	0.0240	0.00413	0.0271	1.5220	Dendritie; crystallized.
11.	Apatite	3.033	2.92-3.25	0.0460	0.01518	0.1113	1.1556	(Glenoree.) Crystalline, fragmentary.
12.	Apatite	3.027	2.92-3.25	0.0260	0.00859	0.0709	1.1316	( " ) Similar to 11.

Phil. Mag. S. 5. Vol. 26. No. 158. July 1888.

### V. On Magnetic Lag. By Thomas H. Blakesley, M.A.\*

IN bringing my views on Transformers before the Physical Society it is my desire to emphasize:—

(1) How the magnetic lag, if it exist, may be measured by

employing dynamometers of low resistance.

(2) That the magnetic lag has a real existence.

(3) That the magnetic lag necessarily accompanies an absorption of work involved in the reversal of polarity in the iron, and how this may be measured.

(4) The points in the general argument where scientific facts are wanting, and the direction which investigation should

take to meet this want.

The possibility of the existence of a magnetic lag renders the problem a different one from that of two coils acting and reacting upon themselves by means of mutual and selfinduction, whose coefficients, being geometrical, are constant.

For the latter problem I gave in the year 1885 a complete solution, but I pointed out that the completeness of the result rested upon the absence of anything in the nature of hysteresis

(a word not then in use) or work done in the field.

The following year Mr. George Forbes, F.R.S., gave what should have been (but for the very poor reporting of the Society of Arts' Journal) a solution of the "secondary generator" problem, treating it as a case of two coils, assuming that "the magnetism of the core varies as the sum of the currents in the two coils;" and the same gentleman has treated the subject again in a recent paper before the Society of Telegraph-Engineers and Electricians, in which he makes the same assumption, and says, referring to the harmonic functions which he attributes to the electrical and magnetic quantities involved, that the existence of magnetic hysteresis would cause departure from the harmonic character, but that, being insignificant so long as the magnetic induction in the iron is not high, its consideration may be omitted; statements which seem rather to evade than to overcome the difficulty.

Mr. Gisbert Kapp, who has done so much good work in the practical development of transformers, also, in my opinion, makes the same assumption, that the state of magnetization in the core coincides with the magnetic stress resulting from

compounding the stresses derived from the two coils.

<sup>\*</sup> Communicated by the Physical Society: read May 12, 1888.

In the view I shall put forward I shall assume:—

(1) That the variations are harmonic.

(2) That the only induction in the secondary coil is derived from the core, and is therefore, as regards phase, in quadrature with the magnetization. As the current in the secondary coil will be considered as producing one of the components of the stress producing magnetization, itself reacting upon the coil, the necessity of introducing a special E.M.F. of self-induction is obviated.

(3) That each turn in either coil embraces the same number

of magnetic lines.

I shall also make use of the following symbols:—

E, the maximum electromotive force of the machine;

I<sub>1</sub>, the maximum value of the current in the primary circuit;

I2, the maximum value of the current in the secondary

circuit;

 $\pi - \theta$ , the angle of phase-difference between the currents; m, the number of turns of wire in the primary coil;

n, ,, secondary coil;

φ, the angle of magnetic lag;

 $r_1$ , the resistance in the primary circuit;

 $r_2$ , ,, , secondary circuit;

are the readings of two dynamometers placed respectively in the primary and secondary circuits, their

constants being A and B, so that  $\frac{I_1^2}{2} = A\alpha_1$ ,  $\frac{I_2^2}{2} = B\alpha_2$ ;

α<sub>3</sub> is the reading of a dynamometer one of whose coils is in the primary, the other in the secondary circuit. Its constant is C.

M is the maximum magnetization.

The magnetic stress produced by each coil is proportional to the current in that coil multiplied by the number of turns in the coil, and is here taken to be that product, called very often the ampere-turns. Its maximum value in the primary coil is  $mI_1$  and in the secondary coil it is  $nI_2$ .

Now the observations on the dynamometers A and B furnish us with a knowledge of  $I_1$  and  $I_2$  in any case; and m and n are details of the construction of the transformer. Thus we

are in possession of the two quantities  $mI_1$  and  $nI_2$ .

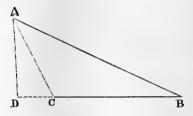
But the three dynamometer observations enable us to determine the angle of phase-difference between the currents, as

or

I have elsewhere explained:-

$$\cos\theta = \frac{\mathrm{C}\alpha_3}{\sqrt{\mathrm{A}\alpha_1\mathrm{B}\alpha_2}} \quad \text{for } \mathrm{C}\alpha_3 = \frac{\mathrm{I}_1\mathrm{I}_2\cos\theta}{2}.$$

We are therefore in possession of the two components of the magnetic stress and of the angle between them. Hence we are virtually in possession of the whole magnetic stress, and its phase relatively to its components. If the resultant is in quadrature with that component which results from the current in the secondary coil, it is in the same phase as the magnetization, which is in quadrature with that component; but not unless this is the case.



Let the line A B represent  $mI_1$  or the magnetic stress in the primary circuit, and let B C represent the magnetic stress in the secondary, and let A B C be the angle  $\theta$ , found as above. Then A C is the resultant magnetic stress.

But the magnetization is in quadrature with BC. Draw AD at right angles to BC. Then CAD represents the magnetic lag, which is seen to vanish if ACB is a right angle. The condition of the existence of lag is therefore that

$$CB < AB \cos \theta$$
,

which in terms of the dynamometer observations is

$$n\sqrt{2 \text{B}\alpha_2} < m\sqrt{2 \text{A}\alpha_1} \frac{\text{C}\alpha_3}{\sqrt{\text{A}\alpha_1 \text{B}\alpha_2}},$$

$$\text{B}\alpha_2 < \frac{m}{n} \text{C}\alpha_3.$$

The observation on the dynamometer in the primary is seen to be eliminated. Thus this question can be tested with two dynamometers only. The amount of lag is represented by the angle CAD. We can easily express its tangent in terms of the three dynamometer observations.

$$\tan \phi = \frac{\text{CD}}{\text{DA}} = \frac{\text{DB} - \text{BC}}{\text{AB} \sin \theta} = \frac{\frac{\text{DB}}{\text{AB}} - \frac{\text{BC}}{\text{AB}}}{\sqrt{1 - \cos^2 \theta}}$$

$$= \frac{\cos \theta - \frac{nI_2}{mI_1}}{\sqrt{1 - \cos^2 \theta}}$$

$$= \frac{\frac{\text{C}\alpha_3}{\sqrt{\text{A}\alpha_1 \text{B}\alpha_2}} - \frac{n}{m} \sqrt{\frac{\text{B}\alpha_2}{\text{A}\alpha_1}}}{\sqrt{1 - \frac{\text{C}^2\alpha_3^2}{\text{A}\alpha_1 \text{B}\alpha_2}}}$$

$$= \frac{\text{C}\alpha_3 - \frac{n}{m} \text{B}\alpha_2}{\sqrt{\text{A}\alpha_1 \text{B}\alpha_2 - \text{C}^2\alpha_3^2}}$$

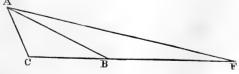
Thus the angle of magnetic lag, if it exist, can be detected with two dynamometers and measured with three.

In dealing yet further with the results furnished by the observations, we must remember that the waxing magnetism has the same inductive effect in producing E.M.F. in each turn of the coils of the two circuits. But we can, from the observation of dynamometer B, say what that E.M.F. per turn is. The whole E.M.F. in the secondary coil is  $I_2r_2$ , consequently the E.M.F. per turn is  $\frac{I_2r_2}{n}$ . Therefore in the primary the total E.M.F. arising from magnetic induction is  $m\frac{I_2r_2}{n}$ .

The current arising from the same source is  $\frac{mI_2}{n} \frac{r_2}{r_1}$  and the magnetizing stress on this account is  $\frac{m^2}{n} \frac{I_2 r_2}{r_1}$ , which must be looked upon as one of the components of the whole magnetizing stress due to the primary current; and this component is in the same phase as the magnetizing stress in the secondary.

Hence, returning to the figure, if we produce CB to F so

that CB : BF :: 
$$n{
m I}_2$$
 :  ${m^2\over n}{{
m I}_2r_2\over r_1}$  ::  $1$  :  ${m^2\over n^2}{r_2\over r_1}$ .



FB is one of the components of AB.

The other component (i. e. that arising from the machine's proper electromotive force) is AF. Hence  $AF = m\frac{E}{a}$ .



It follows that the electromotive force E, which the machine is exerting, may be thus determined by means of the dynamometer observations.

$$AF^{2} = AB^{2} + BF^{2} + 2AB BF \cos ABC,$$

$$\frac{m^{2}E^{2}}{r_{1}^{2}} = m^{2}I_{1}^{2} + \left(\frac{m^{2}}{n^{2}}\frac{r_{2}}{r_{1}}\right)^{2}n^{2}I_{2}^{2} + 2mI_{1}\frac{m^{2}}{n^{2}}\frac{r_{2}}{r_{1}}nI_{2}\cos\theta,$$

$$\therefore E^{2} = r_{1}^{2}I_{1}^{2} + r_{2}^{2}I_{2}^{2}\frac{m^{2}}{n^{2}} + 2r_{1}r_{2}\frac{m}{n}I_{1}I_{2}\cos\theta,$$

$$= r_{1}^{2}2A\alpha_{1} + \frac{m^{2}}{n^{2}}r_{2}^{2}2B\alpha_{2} + 4r_{1}r_{2}\frac{m}{n}C\alpha_{3},$$

$$= 2\left\{r_{1}^{2}A\alpha_{1} + r_{2}^{2}\frac{m^{2}}{n^{2}}B\alpha_{2} + 2r_{1}r_{2}\frac{m}{n}C\alpha_{3}\right\}.$$

Another interesting magnitude is AC, or the total impressed magnetic force.

$$\begin{split} & \text{AC}^2 \!=\! \text{AB}^2 \!+\! \text{BC}^2 \!-\! 2 \text{AB BC } \cos \theta, \\ &= m^2 \text{I}_1^2 + n^2 \text{I}_2^2 \!-\! 2 m n \text{I}_1 \text{I}_2 \cos \theta, \\ &= 2 m^2 \text{A} \alpha_1 + 2 n^2 \text{B} \alpha_2 \!-\! 4 m n \text{C} \alpha_3, \\ &= 2 \left\{ m^2 \text{A} \alpha_1 + n^2 \text{B} \alpha_2 \!-\! 2 m n \text{C} \alpha_3 \right\}. \end{split}$$

By means of this we may calculate what current should be passed through the primary circuit, the secondary being open, to produce the same state in the core.

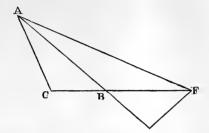
But perhaps the most interesting point to men of science and to civil engineers is the question of power. We may approach it thus perhaps in the simplest way.

By dropping a perpendicular from F upon AB produced we easily see that

AF cos BAF=BF cos ABC+AB.

Multiplying through by AB we have

 $AFAB\cos BAF = ABBF\cos ABC + AB^2$ .



Substituting the electric quantities for the geometrical,

$$\frac{mE}{r_1}mI_1\cos BAF = mI_1\frac{m^2}{n^2}\frac{r_2}{r_1}nI_2\cos\theta + m^2I_1^2$$
;

multiply through by  $\frac{r_1}{2m^2}$ ,

$$\frac{\mathrm{EI}_{1}\cos\mathrm{BAF}}{2} = r_{2}\frac{m}{n}\frac{\mathrm{I}_{1}\mathrm{I}_{2}\cos\theta}{2} + \frac{r_{1}\mathrm{I}_{1}^{2}}{2}.$$

But the term on the left is the expression for the total power, and those on the right hand may be expressed in terms of the dynamometer observations.

Thus the total power

$$= r_1 \mathbf{A} \alpha_1 + r_2 \frac{m}{n} \mathbf{C} \alpha_3.$$

The first term here is obviously the power at work heating the primary coil.

 $r_2$ B $a_2$  is as obviously the power heating the secondary coil.

If, therefore, we write the total power

$$= r_1 \mathbf{A} \boldsymbol{\alpha}_1 + r_2 \mathbf{B} \boldsymbol{\alpha}_2 + r_2 \left\{ \frac{m}{n} \mathbf{C} \boldsymbol{\alpha}_3 - \mathbf{B} \boldsymbol{\alpha}_2 \right\},\,$$

we see that the power involved with the magnetic lag is

$$r_2\left\{\frac{m}{n}\mathrm{C}\alpha_3-\mathrm{B}\alpha_2\right\},$$

the form showing that it disappears if the lag does so.

Thus we are led to the conclusion that a magnetic lag involves a loss of power, and any loss of power due to molecular action in the core taking place in the course of the alternations of magnetization must necessarily produce lag.

Now if the changing magnetization does work it must do it against a force, and this force must be of the character which of itself would produce magnetization, i. e. magnetic

force. Just as when a body moving in a medium does work in the medium, it does so by calling into being, or inducing, a force, viz. friction; force being that sort of magnitude which acting upon a body produces motion.

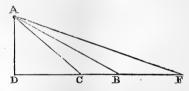
By analogy alone, therefore, we may infer that when changing magnetization is a continuous source of absorbed work, the changing magnetization induces what would itself produce magnetization, that is an induced stress acting in opposition to the direction of the change in the magnetization.

This may perhaps be allowed; but it may be urged that there is plenty of magnetic stress already, impressed by the currents; why should not the changing magnetization work on this? The answer to this objection is that if there be no other stress but that impressed from outside, then the phase of the magnetization will be in the same phase, and therefore the increase of magnetization will be in quadrature with the stress, and hence no work will be continuously absorbed. For though through some phases work may be done in such a case, this is always recoverable and recovered in a complete period; a proposition which I have stated and proved in my papers upon Alternating Currents in 1885.

I apprehend, therefore, that besides the stresses AB BC we have another induced stress in quadrature with the magnetization, because called into being by its increase, and

therefore in the same phase as FB or BC.

Let BC, therefore, be produced until it meets in D the line AD drawn at right angles to BC.



Then AD will be the effective magnetic stress, i. e. that magnetic stress which, maintained with a steady current, will produce the actual magnetization; hence, if M is the maximum magnetization,

$$\frac{4\pi AD}{\rho} = M,$$

where  $\rho$  is called the magnetic resistance. Thus

$$AD = \frac{M\rho}{4\pi}.$$

If 2T is the period of alternation,  $\frac{\pi M}{T}$  is the maximum rate of increase of M.

$$N\frac{\pi M}{T} = DC$$
,

N may be called the coefficient of magnetic self-induction.

Under the exigencies of a certain temporary nomenclature CD might be called the Foucault-Ampere turns existing in the core itself.

Substituting for M in terms of AD,

$$DC = \frac{N\pi}{T} \frac{4\pi AD}{\rho},$$

$$\frac{DC}{AD} = \tan \phi = \left\{ \frac{4\pi^2}{T_0} \right\} N.$$

or

I have explained above how tan  $\phi$  may be obtained from the dynamometer observations. We may therefore employ this formula for the determination of the value and constancy of N, if we can rely upon the values of T obtained by observation at the time, and of  $\rho$  known otherwise.

The constancy of  $\rho$  obtains so long as magnetization can keep pace with magnetic stress. These conditions are fairly well understood, and AD must not exceed the stress representing the limiting one. Thus it will be well to know AD

$$\begin{aligned} \text{AD=AB sin } \theta = m \text{I}_1 \sqrt{1 - \cos^2 \theta}, \\ = m \sqrt{2 \text{A} \alpha_1} \sqrt{1 - \frac{\text{C}^2 \alpha_3^2}{\text{A} \alpha_1 \text{B} \alpha_2}}, \\ = \sqrt{2}. m. \frac{\sqrt{\text{A} \alpha_1 \text{B} \alpha_2 - \text{C}^2 \alpha_3^2}}{\sqrt{\text{B} \alpha^2}}. \end{aligned}$$

I think, therefore, experiment should move in the following direction. The constancy or the reverse of N under varying speeds should be first determined by experiments with currents so small or coils so few that the magnetic resistance  $\rho$  may be safely assumed constant. For this purpose it would be necessary to employ some speed-indicator.

Professor Forbes, F.R.S., in his paper upon transformers, already quoted, says that the existence of hysteresis would cause a departure from the harmonic character of the motion,

but that the effects are small and negligible.

If N, however great, remains constant, the harmonic character of the variation is maintained. But if experience showed that induced stress varies as the square or higher power of the rate of change of magnetization, then indeed a serious modification would take place, and this would be likely if the neighbourhood of saturation were reached.

In the foregoing investigation I have represented magnetic stress as of the order Current, and the formulæ I have introduced hitherto will bear this convenient form of expression; but strictly speaking it is of the order Field, and when we wish to settle the dimensions of N we must take this into account. The M of the work is really of the order Moment or  $[l^{\frac{5}{2}}t^{-1}m^{\frac{1}{2}}]$ . Now the rate of increase of Moment multiplied into N is equal to Field or  $[l^{-\frac{1}{2}}t^{-1}m^{\frac{1}{2}}]$ ;

$$N \frac{\left[l^{\frac{5}{2}}t^{-1}m^{\frac{1}{2}}\right]}{t} = \left[l^{-\frac{1}{2}}t^{-1}m^{\frac{1}{2}}\right],$$

$$N = \left[l^{-3}t\right].$$

The actual experiments, which I now bring to the notice of the Society, were carried out at the works of Messrs. Nalder, Brothers & Co., of Westminster, and I am greatly indebted to these gentlemen themselves, and to Mr. Crawley and Mr. Mott for their assistance in making them, for they freely placed their steam-power, their electrical power, and their intellectual power at my disposal.

These experiments had no other object than to test the question of the existence of magnetic lag by dynamometers,

and to measure the angle of lag.

The machine employed and the transformer were of the Kapp forms. The numbers of turns of wire in the two coils had been ascertained for me by Mr. Crawley. They were 100 and 12 respectively.

Considering the considerable differences in the relations of the currents, the constancy of the angle of lag appears to me to point to a simple law connecting it with the magnetization.

There was no very accurate speed-indicator employed, and the speed was approximately the same in the first six experiments. In the seventh experiment the speed was purposely much diminished, by about one third of that in the former cases, and in this experiment alone does the lag appear at less than 5°.

				,			
No. of Experi- ment.	$egin{aligned} \mathbf{A} \mathbf{a}_1 &= & & & \\ & \mathbf{I_1}^2 & & & & \\ & 2 & & & & \end{aligned}$	$egin{array}{c} \mathbf{B}\mathbf{z}_2 = \ \mathbf{I}_2^{\ 2} \ 2 \end{array}.$	Cæ₃.	$\frac{m}{n}$ $\mathbf{C}\mathbf{z}_3$ .	θ.	φ.	$\sqrt{A}\alpha_1\sin\theta$ .
1	33.29	52.65	10.37	86.46	75° 40′	5°43'	5.590
2	34.43	59.74	11.50	95.83	75 19	5 38	5.676
3	37.09	92.14	17.34	144.50	72 45	6 25	5.816
4	70.38	86.06	17.43	145.22	77 4	5 21	8.176
5	81.17	81.00	17.21	143.42	77 45	5 24	8.804
6	84.97	29.03	7.83	65.26	80 56	5 4	9.103
7	8.21	101.59	14:31	119.26	60 17	4 50	2.488
No. of Experiment.	$r_1$ .	$r_2$ .	$rac{{ m I_1}^2}{2} r_1.$	$rac{{ m I_2}^2}{2}r_2$ .	Power of internal magnetic work = H.		$rac{ ext{H}}{ ext{A} oldsymbol{arphi}_1 \sin^2  heta}.$
1	2.01	2.51	66.91	132.15	84	96	2:72
2	,,,	2.36	69.20	140.99	85.17		2.64
3	"	1.96	74.55	180.59	102	63	3.03
4	"		141.46				
5	"	2.87	163.15	232.47	179	15	2.31
6	,,	4.77	170.79	138.47	172	82	2.09
7	n	0.72	16.50	73.14	12·	73	2.06

#### VI. On Electromotive Forces of Contact. By Charles V. Burton, B.Sc.\*

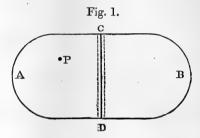
THE principal object of this paper is to discuss the seats of the electromotive forces developed by the contact of conductors, and by considering the transformations of energy which occur when two insulated conductors are brought into contact, an attempt is made to give a logical demonstration of some of the views put forward. In the latter part of the paper a description is given of some experiments on the nature of the electrification of non-conductors by contact or friction.

When two conductors are brought into contact, an electromotive force (E) is set up between them, which drives

<sup>\*</sup> Communicated by the Physical Society: read April 28, 1888.

electricity across the junction, until the difference of their potentials\* has an E.M.F. equal and opposite to E. I shall assume that E is always the same so long as we keep to the same substances and the same temperature; and also that when electric equilibrium has been established each conductor is at a uniform potential throughout, except very near the junction, and that there the potential changes in general by a finite amount as we pass through a layer of very small but finite thickness, which includes the surface of separation.

Let the two conductors A and B (fig. 1) be in contact over



the surface CD, and let the difference of their potentials be The potential is constant throughout the extent of A, and also throughout the extent of B, except within a very thin layer including the surface CD, which may be called the layer of variable potential, and where the potential may be supposed to change continuously from that of A to that of B as we pass from one side of the layer to the other. consider the distribution of electricity on the system. tric masses will be distributed on the external surfaces of A and B, but not within these surfaces, except within the layer of variable potential. Here the distribution evidently depends upon the thickness of the layer, the law of variation of potential across the layer, and the specific inductive capacity of A and B. This last quantity is evidently the true or finite specific inductive capacity, and not the apparent or infinite specific inductive capacity which conductors appear to have in ordinary electrostatic experiments; for in the latter case the electric potential energy of the layer CD would be infinite.

It is usually supposed that the contact E.M.F. between two conductors is due to some molecular action between them.

<sup>\*</sup> Wherever the potential of a conductor is spoken of, the potential at any point throughout its volume is intended, and not the potential at a very near external point. I must apologise for this unusual use of the term.

And my first point is to show that this action is confined to

molecules within the layer of variable potential.

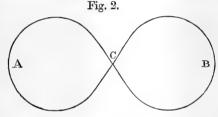
For consider a particle P (fig. 1) within the conductor A, so that all around P the potential is constant. Then if P takes part in any way in maintaining a difference of potentials between A and B, it must in turn be reacted on by the electric forces which tend to equalize the potential throughout the system. Now, the only forces tending to equalize the potential are the attractions and repulsions *inter se* of the electric masses distributed on the conductors; and the particle P being situated in a region where the potential is constant, the electric force at P is zero.

Therefore P suffers no reaction from the electric masses of the system and cannot, therefore, play any part in maintain-

ing the difference of potential.

Hence the molecular action which gives rise to a contact E.M.F. between two conductors is confined to the immediate neighbourhood of the junction.

Now, suppose that two conductors A and B (fig. 2), whose



contact-difference of potentials is P, are originally at the same potential, and are then brought into contact at C. As soon as this is done an E.M.F. E (= -P) will act between A and B, and will drive electricity across the junction at C, until the difference of potentials of A and B becomes equal to P.

At the beginning of the operation, when contact first occurs, there is no E.M.F. opposed to E, so that when E drives a quantity dM of electricity across the junction, the work done is EdM. As there is no opposing E.M.F. to be overcome, the whole of this work is spent in producing heat,

according to the Joule effect.

At a later stage, when the difference of potentials has become (say) p, the total E.M.F. between the conductors = E + p; p being of course of the opposite sign to E. Hence, when the quantity dM crosses the junction, the work (E+p)dM is spent in producing the Joule effect; while the electric potential energy of the system increases by -pdM; so that the total work done on dM by the E.M.F. E=EdM.

Hence, if in order to establish the difference of potentials P between A and B, the quantity M of electricity must cross the junction, the work done by the E.M.F. E during the operation is E.M., half this work being spent in producing the Joule effect, and half in raising the electrostatic potential energy of the system.

But the E.M.F. E is due to molecular action in the immediate neighbourhood of the junction, and, therefore, when the E.M.F. E does work by causing a displacement of electricity, a corresponding amount of molecular energy is

absorbed at the junction.

Now, E being finite, suppose that the surface of contact at the junction C (fig. 2) is very small, and that the electrostatic capacities of the conductors are very great. Then M will be very great, and so will EM. In fact, keeping the junction as small as we please, we may increase EM indefinitely by increasing the electrostatic capacity of the system.

But, by hypothesis, the E.M.F. E will always be maintained so long as we keep to the same substances, and maintain

them at the same constant temperature.

Hence, when the E.M.F. E does work, the molecular energy absorbed is of such a nature that it can be supplied in indefinite amount by a small finite junction maintained at a constant temperature.

There are only two kinds of energy which fulfil this condition: -(1) Heat; (2) Chemical action at the junction.

First, suppose that the conductors A and B (fig. 2) are incapable of acting chemically upon one another. Then for every quantity dM of electricity which crosses the junction in the direction of the E.M.F. E, this E.M.F. does work EdM, and an equivalent amount of heat is absorbed at the junction. And, conversely, if electricity dM cross the junction in the opposite direction, work will be done against those molecular agencies at the junction which maintain the E.M.F. E, *i. e.* the work done on the E.M.F. E will appear in the form of heat.

Hence, the true contact E.M.F. between two chemically inactive conductors is equal to their coefficient of the Peltier

effect expressed in absolute measure.

An argument sometimes advanced against this proposition is substantially as follows (I quote from Professor Lodge's paper in the Phil. Mag. for April 1885, p. 260):—" When Q units of electricity are transmitted against a force E, work EQ is done; also when they are transmitted up a difference of potential  $V^1-V$ , work Q ( $V^1-V$ ) is done; but in an open

circuit containing an electromotive junction, V¹-V is produced by and is equal to E. Hence, at an electromotive junction no work need be done by a current; in other words, the existence or non-existence of a Peltier effect has nothing to do with the existence or non-existence of a local E.M.F."\*

But although on an open circuit, there are two equal and opposite E.M.F.'s at the junction, and consequently there is no resistance to the flow of electricity in either direction, still the E.M.F. which acts in the direction of the flow will

do work upon the opposing E.M.F.

A mechanical example may make this clearer. If a particle be acted upon by two equal and opposite forces, each of one dyne, the smallest possible force will be able to displace the particle in any direction; but if the particle be displaced one centimetre in the direction of one of the dyne-forces, this force will do just one erg of work upon the other force.

Now, at the junction between two chemically inactive conductors, the two E.M.F.'s are (1) an E.M.F. E due to a tendency to absorption of heat-energy at the junction, and transformation of the absorbed energy into electrical energy by displacement of electricity across the junction, and (2) an E.M.F. P = E due to difference of potentials between the conductors.

Hence, if electricity M cross the junction in the direction of the E.M.F. E, heat-energy EM is absorbed in order to drive the quantity M up the step of potential; while if electricity M cross the junction in the opposite direction, energy EM will be given out in descending the step of

potential and will appear in the form of heat.

Returning now to the consideration of the conductors A and B (fig. 2), suppose that they are capable of acting chemically upon one another. In this case the energy required to establish the difference of potentials between A and B may be supplied at the junction either in the form of heat absorbed there or chemical action taking place. For the sake of simplicity let the Peltier E.M.F. be zero, so that we have only to deal with a chemical E.M.F. It will also be simplest to consider one of the conductors to be a solid and the other a liquid, so that any chemical action which may take place will not modify the nature of the subtances in contact.

For every quantity M of electricity which crosses the junction in the direction of the E.M.F. chemical energy EM will be absorbed, i. e. an amount of chemical action proportional to

M will take place.

This is in accordance with Faraday's Electrolytic Law.

<sup>\*</sup> Professor Lodge refutes this by a hydrostatic analogy.

Professor Lodge considers that the E.M.F. between chemically active substances is due to a tendency to chemical action. But mere tendency to chemical action at a finite junction could not be the source of an indefinite amount of energy, and could not, therefore, account for the phenomena in the case discussed above. There must be actual chemical action. It appears in fact (excluding all idea of a Peltier E.M.F.) that when two chemically active conductors are brought into contact, electricity in general crosses the junction, and establishes a difference of potential between them, and the amount of chemical action which takes place is precisely the equivalent of the electricity which crosses the junction determined in accordance with Faraday's Electrolytic Law.

Let K=number of absolute units of energy evolved when one gram of (say) the substance A enters into the kind of combination which takes place in the case considered. Let k=number of grams of A which enters into combina-

tion per unit flow of electricity.

Then for every unit of electricity which crosses the junction, E units of chemical energy are absorbed; ... E/K grams of A are dissolved.

# $\therefore$ E/K=k or E=kK.

That is, the E.M.F. is equal to the energy of combination of one

electrochemical equivalent.

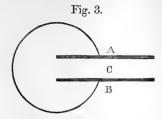
Of course this is only the case where all the energy of the chemical action is converted into electrical energy; as in the case of pure zinc dipped in dilute sulphuric acid. From this it follows that in the case of the typical cell, for instance, where pure zinc and pure copper are immersed in dilute sulphuric acid, the principal E.M.F is at the contact of the zinc and acid, an opposing E.M.F. being set up at the contact of acid and copper.

If we construct a cell consisting of zinc and carbon dipping in dilute  $H_2SO_4$ , there will be no power of chemical action at the liquid-carbon junction, so that the only E.M.F. there is a Peltier E.M.F. Neglecting Peltier E.M.F.'s altogether, the E.M.F. of such a cell would be equal to that of the zinc-

liquid junction.

The apparent contact E.M.F.'s of metals, as measured in air, must be due chiefly to the air-metal contacts, since a metal-metal contact can only be the seat of a Peltier E.M.F. It also appears that if the apparent E.M.F. between two metals were measured inductively in some chemically inactive gas (or liquid), the result would be the sum of three Peltier E.M.F.'s, and would probably be small. There even seems to be some reason for supposing it to be zero.

For consider a circuit consisting of two metals A and B (fig. 3) and an inert gas C, all at the same temperature.



Suppose that there is on the whole a finite E.M.F. in the circuit ACBA, i. e. that the potential of the gas C varies as we pass from the plate A to the plate B. Now, it is evident that if the gas C has any trace of conductivity, or any power whatever of equalizing potentials by convection, a feeble current will flow continuously around the circuit ACBA, and will derive its energy from absorption of heat at one or more of the junctions, which would be a violation of the Second Law of Thermodynamics. If the metal A were furnished with points as fine as possible, and if these points were brought within an extremely small distance of B, they would greatly favour any conductive or convective tendency that might exist; and if by such an arrangement a convective discharge of only one molecule of electricity in a century were established, it would constitute a violation of the Second Law of Thermodynamics.

If we admit that in an inert gas C the difference of potential between the layers in contact with A and B is finite, we must assume that the gas is an absolutely perfect insulator for such an E.M.F. Even if this property is assumed it does not follow that Volta's Law is inapplicable to the case of

gases and metals.

I have endeavoured to show how a Peltier E.M.F. depends on a tendency to absorb heat-energy and convert it into electrical energy. Now from the law of successive contacts of chemically inactive conductors, it is evident that, the temperature being fixed, we can connect with each substance a constant (called its "Peltier-constant") such that the E.M.F. between any two inactive conductors is equal to the difference of their respective constants, which is only another way of stating Volta's Law.

Now it seems not unlikely that the Peltier constant of a given conducting substance, at a given temperature, depends only on the size, form, &c. of its molecules, and the nature of their heat-motion; and, if so, each non-conductor should also have

its Peltier constant, since the conditions are essentially the same in the two cases.

Thus the law of successive contacts might hold for chemi-

cally inactive non-conductors as well as for conductors.

It might even be that the law is universally true so far as Peltier E.M.F.'s only are concerned; but of course these are only speculations.

The following are some analogous properties of Peltier E.M.F.'s and chemical E.M.F.'s arranged respectively in

parallel columns:-

#### PELTIER E.M.F.

1a. When the two substances originally at the same potential are brought into contact an E.M.F. E<sub>1</sub> is established across the junction; this E.M.F. continues to displace electricity across the junction until the E.M.F. due to difference of potentials— - E<sub>1</sub>.

2a. The energy required to establish the difference of potentials is supplied by heat absorbed at the

junction.

3a. For every quantity M of electricity which crosses the junction in the direction of the E.M.F. E<sub>1</sub>, a quantity of heat-energy E<sub>1</sub>M is absorbed at the junction.

4a. For every quantity M of electricity which crosses the junction against the E.M.F. E<sub>1</sub>, heat-energy E<sub>1</sub>M is given out at the junction.

5a. 'Ine

tion a heat absorbed at the juncthe e uring the operation (1a) is whic quivalent of the electricity min h crosses the junction, deterlawed in accordance with the s of the Peltier effect.

#### CHEMICAL E.M.F.

1b. When the two substances originally at the same potential are brought into contact an E.M.F.  $E_2$  is established across the junction; this E.M.F. continues to displace electricity across the junction until the E.M.F. due to difference of potentials  $= -E_2$ .

2b. The energy required to establish the difference of potentials is supplied by chemical action taking

place at the junction.

3b. For every quantity M of electricity which crosses the junction in the direction of the E.M.F. E<sub>2</sub>, a quantity of chemical energy E<sub>2</sub>M is absorbed at the junction.

- E<sub>2</sub>M is absorbed at the junction.

  4b. For every quantity M of electricity which crosses the junction against the E.M.F. E<sub>2</sub>, energy E<sub>2</sub>M is given out at the junction, and appears either as chemical-energy (electrolysis) or as heat.
- 5b. The chemical action at the junction during the operation (1b) is the equivalent of the electricity which crosses the junction, determined in accordance with Faraday's Electrolytic Law.

Sir W. Thomson has deduced a lower limit to the size of atoms by a method which is well known. Professor Lodge points out that the limit cannot be assigned with certainty, until the true contact-difference of potentials of the substances concerned is known. But there is another point to be considered. The method assumes that there is a kind of affinity between the molecules of the two metals concerned; that on contact being made, this affinity gives rise to an E.M.F. which establishes a difference of potential, the necessary

energy being furnished by the partial satisfaction of the said affinity. The method further assumes that when the metals are fused together it is this same affinity which, being satisfied as completely as possible, gives rise to an evolution of heat. But if (as appears from what precedes) the energy required to produce the difference of potentials is supplied by absorption of heat at the junction, and if the contact E.M.F. is due to a tendency to convert heat-energy into electrical energy, then the heat evolved on fusing the metals together can have no direct connexion with E.M.F.'s of contact, and the method would not apply to the case of two metals.

It would, however, obviously apply where the E.M.F. was due to chemical affinity, as in the case of zinc and oxygen proposed by Professor Lodge (Phil. Mag. May 1885, p. 363). In all these investigations the electrostatic capacities are calculated on the assumption that the specific inductive capacity of the conductors is unity. I have not been able to find any

experimental justification for this assumption.

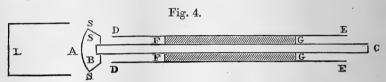
# Electrification of Non-conductors.

When two non-conductors are brought into contact, there are other sources of energy which may cause electrification. For if the bringing of two free surfaces into contact, or the striking or rubbing of the bodies together, should give rise to electrification, the charges so produced would remain separated, owing to the insulating properties of the substances. This source of electrification is absent in conductors, as any electrification produced between them by sudden violence would be destroyed by conduction, the final difference of potentials between the bodies being always that due to a definite contact E.M.F.

The difference between the two cases may be illustrated by considering the case of a spring. If a force be applied to the spring a definite compression will ensue, supposing that there is no friction; and if by any temporary impulse the compression be increased or diminished, it will regain its former value when the impulse ceases to act. The inverse of the strength of the spring represents the capacity of the system, the force compressing the spring the E.M.F. of contact, the distance through which the spring is compressed the quantity of electricity displaced, and the potential energy of the compressed spring the electrostatic potential energy of the two conductors.

If we suppose compression or extension of the spring to be accompanied by friction, a compression effected by a sudden shock will be maintained. This illustrates what perhaps

takes place with non-conductors. In order to test which view is the more correct, I have made a few experiments on the electrification of glass and ebonite when dipped into mercury. This method of experimenting seemed to offer several advantages. The mercury being permanently connected to earth was always at a known potential (zero), and it was only necessary to measure the charge of the ebonite or glass. Then, again, contact was obtained over the whole surface submerged, with very little mechanical violence when desired; and the conditions of contact could be considerably varied by using more or less suddenness and violence and longer or shorter duration of contact.



The ebonite or glass employed consisted of a small circular slab S (fig. 4) with a convex surface A, which was attached to one end of a rod BC of the same material. This rod was encased in a brass tube DE, inside which it was fastened by means of packing FG. The length BF of ebonite or glass served to insulate the slab A. In the case of the glass the length BF was varnished. The charge on A was measured by means of the conductor L connected to a Thomson electrometer. A was placed near to L, which was put to earth and then insulated. On withdrawing A, a deflection was produced proportional to the charge on A. The movement of A was controlled by making the tube DE slide in metal bearings between fixed stops. The tube DE being of metal, no electrification was produced by friction in the bearings. The following results were obtained:—

		(a) Ebon	ite and M	<i>lercu</i>	ry.			DEFLECTION.
Dipped or	ice and	quickly	withdraw	n.				+10  to + 12
22	99	very qui	ckly with	ıdrav	$\mathbf{v}\mathbf{n}$			+15
,, fo	r 10"	quickly	withdraw	n.		•		+15 + 7 to +15
"	15"	,,	"					+ 6  to + 10
22 23	30"	,,	22	•	•			+ 6  to + 13
	60"	,,	"	•		•	,	+ 5  to + 9
30 rapid	splashe	es in the	mercury				٠.	<b>-</b> 6
50 not v	ery rap	id splash	es in the	merc	cur	y		+ 7
100 rapid		"	"	. ,	,		•	-11
200 ,,		"	22	,	,		•	-10

		(1)	o)	Glo	ıss	and	l M	[erc	ury			DEFLECTION.
Dip	ped or	nce quietly			•							+ 6 to + 10
20	rapid	splashes				•						<b>–</b> 7
50	"	22	•	•	•	•	•	•	٠	•	٠	- 1
60	"	27	•	•	•	•	•	•	•	•	•	<b>-</b> 6
90	22	"	٠	•	•	•	٠	•	•	٠	•	+ 4
100	22	"	٠	•	•	•		•	•	•		<b>–</b> 0

The above results, it will be seen, are very irregular, owing no doubt to the fact that all the circumstances of contact could not be accurately known. These irregularities, and especially the variable sign of the electrification, make it clear that the effects are not due to a true and definite contact E.M.F., but are dependent in some degree on the manner in which the surfaces are brought together and separated. The experiment of Canton in 1753 (where the rough and polished parts of a glass tube became oppositely electrified when rubbed with the same cloth) seems to point in the same direction.

Professors Ayrton, Schuster, S. P. Thompson, and J. Perry discussed the points raised, and it was considered that direct experiment on contact electromotive force in a very perfect vacuum could alone decide the question.

This experiment seems almost as impracticable as a direct measurement of the size of a molecule. Yet the two questions may be equally capable of solution by inductive reasoning. The question is whether the reasoning given above is or is not conclusive.—C. V. B.

VII. On Thermochemical Constants. By Spencer Umfreville Pickering, M.A. Oxon, Professor of Chemistry at Bedford College\*.

THE existence, amongst thermochemical data, of certain quantities which are constant, or nearly constant, cannot be denied.

We have in the first instance the fact that the heat of neutralization is in the majority of cases independent of the nature of the acid and the alkali concerned; and a simple explanation of this may be found, as I have shown (Chem. Soc. Trans. 1887, p. 593), in the complete saturation of the

<sup>\*</sup> Communicated by the Author, having been read before the Chemical Society.

residual affinity of one of the radicals in the molecules concerned by the excess of water used to dissolve them. When, again, metals are acted on by excess of water (or of weak hydrochloric acid), the heat evolved, though not an absolutely constant quantity, is approximately so in many cases, especially when the cases taken refer to metals belonging to the same group. The chemical reactions involved are of a precisely similar nature in each case; and the small differences which exist are easily accounted for by the differences in the constitution of the metallic molecules themselves.

The heat of formation of any given metallic salt in solution is calculated from the heat evolved in reacting on the metal with water, the heat of neutralization, and the heat of forma-

tion of the acid and water; thus

$$Na$$
,  $Cl = (Na, aq.) + H$ ,  $Cl$ ,  $aq. + NaOH$   $aq.$ ,  $HCl$   $aq.$ ;

all of which quantities, except the first (Na, aq.), are identical, or else constants, whatever metal be taken. Hence there is a constant and comparatively small difference between the heat of formation of solutions of similar salts of different metals:—

$$K$$
,  $Cl$ ,  $aq. -K$ ,  $NO_3$ ,  $aq. = Na$ ,  $Cl$ ,  $aq. -Na$ ,  $NO_3$ ,  $aq.$ 

In calculating the heat of formation of salts in the solid state the same equations hold good, except that there must be subtracted the heat of dissolution of the salt in question. As the heat of dissolution of similar salts of different metals is often identical within a thousand or a few hundred calories—a quantity which, though large in proportion to the heat of dissolution itself, is but insignificant in comparison with the heat of formation of the salt—the same constant differences will very nearly obtain in the heat of formation of the solid salts.

Again, the substitution of similar radicals in gaseous members of an homologous series, such as the hydrocarbons and their derivatives, gives rise to the same heat-development.

All these constants or semi-constants present no difficulties whatever to our minds; but there is another class of constants

where the case is very different.

Thomsen's second volume of Thermochemical Researches, dealing with the combinations of the non-metals, abounds with instances where the heat evolved in two somewhat similar reactions is a multiple of some common constant: thus,

Iodic acid . . . .  $I_2$ ,  $O_6$ ,  $H_2$ ,  $aq. = 111,590 = 3 \times 37,197$ , Periodic acid . . I,  $O_6$ ,  $H_5$ ,  $aq. = 184,400 = 5 \times 36,880$ . Hence substitution of I for  $H_3 = 72,810 = 2 \times 36,405$ .

The symbols refer to molecular oxygen and hydrogen, and solid iodine.

Now when we come to consider what the real reactions taking place in the two cases are, namely:—

(a) 2(I, O<sub>3</sub>, H)+2(IO<sub>3</sub>H, aq.) -I, I-3(O, O)-H, Hheat of fusion of 254 grams iodine + heat of liquefaction of 96 grams oxygen and 2 grams hydrogen,

(b) I, O<sub>6</sub>, H<sub>5</sub> + IO<sub>6</sub>H<sub>5</sub>, aq.  $-\frac{1}{2}$ (I, I) -3(O, O)  $-2\frac{1}{2}$ (H, H) — heat of fusion of 127 grams + heat of liquefaction of 96 grams oxygen and 5 grams hydrogen,

it is impossible to see how the algebraic sums of these various chemical and physical quantities can be multiples in the proportion of 3:5, or in any other proportion, of any common constant, unless it be by mere chance; nor can the case be simplified by regarding periodic acid as formed by the direct substitution of H<sub>3</sub> for I, which it certainly is not.

The instances brought forward by Thomsen of numbers which are multiples of constants may be classed under three

heads :--

A. The heat of formation of compounds from their constituent elements, either in the presence of excess of water or otherwise.

- (1) Iodic and periodic acids quoted above.
- (2) 2NO, O, aq. =  $36,330 = 1 \times 36,330$ , 2NO, O<sub>3</sub>, aq. =  $72,970 = 2 \times 36,485$ .
- (3) P, O<sub>4</sub>, H<sub>3</sub>\*=300,080= $4 \times 75,020$ , P, O<sub>3</sub>, H<sub>3</sub> =  $224,630=3 \times 74,877$ .
- $\begin{array}{lll} \text{(4)} & \text{S, O}_2 &= 77,280 = 6 \times 12,880, \\ & \text{S, O}_3 &= 103,240 = 8 \times 12,905, \\ & \text{S, O}_4, \text{H}_2 = 192,920 = 15 \times 12,861. \end{array}$
- (5)  $2SO_2$  aq., O = 53,520,  $2S_2O_2$  aq., O = 53,490.
- (6) 2CO, O, aq. =73,920, CO, O, aq. =73,840.
- (7) Sn, O<sub>2</sub>, H<sub>2</sub>O=133,500=2 × 66,750, Sn, O, H<sub>2</sub>O = 65,410=1 × 65,410.

<sup>\*</sup> This refers to the heat of formation of the molten acids; the numbers obtained with solutions of the acids are 4×76,320 and 3×75,860 respectively, but these can scarcely be regarded as forming an independent instance. The heat of dissolution of the two molten acids are naturally positive quantities not differing much from each other, and both very small in comparison with the heat of formation of the acids.

(8) Fe, 
$$\text{Cl}_2 = 82,050 = 3 \times 27,350$$
,  
 $\text{Fe}_2$ ,  $\text{Cl}_6 = 192,080 = 7 \times 27,440*$ ,  
 $\text{Fe}_2\text{Cl}_6$ ,  $\text{aq.} - 2(\text{FeCl}_2,\text{aq.}) = 27,560$ .

(9) Fe, O, 
$$H_2O = 68,280 = 5 \times 13,656$$
,  
Fe<sub>2</sub>, O<sub>3</sub>,  $3H_2O = 191,150 = 14 \times 13,654$ .

B. Differences between the heat of formation of analogous compounds.

(10) 
$$H_2$$
,  $Cl_2 - H_2$ ,  $Br_2^{gas} = 19,480 = 3 \times 6493$ ,  $H_2$ ,  $Br_2^{gas} - H_2$ ,  $I_2^{gas} = 25,698 = 4 \times 6425$ .

(11) N, H<sub>4</sub>, Cl 
$$-$$
H, Cl, aq. = 36,472,  
N, H<sub>4</sub>, Br $-$ H, Br, aq. = 36,972,  
N, H<sub>4</sub>, I  $-$ H, I, aq. = 36,142.

(12) 
$$P_2$$
,  $O_5 = 369,900 = 5 \times 73,980$ ,  
 $As_2$ ,  $O_5 = 219,380 = 3 \times 73,130$ ,  
 $As_2$ ,  $O_3 = 154,670 = 2 \times 77,330$ .

C. Numerical relations between similar reactions, and between the differences between similar reactions, where more than one product is formed.

(13) 
$$6\text{KOH aq.} + 6\text{Cl} = 3\text{KCl aq.} + 3\text{KOCl aq.} + 3\text{H}_2\text{O}$$
  
=  $73,855 = 3 \times 24,618$ .  
 $6\text{KOH aq.} + 6\text{Cl} = 5\text{KCl aq.} + \text{KO}_3\text{Cl aq.} + 3\text{H}_2\text{O}$   
=  $97,945 = 4 \times 24,486$ .

There is not one of these sets of quantities (except perhaps the actions of chlorine on potash, 13, and the formation of the haloid acids, 10) in which the actions compared are so simple or so strictly analogous, that we might reasonably expect the sum total to be made up of the same constants.

In some cases, indeed, it is apparent that Thomsen has been led astray by his eagerness to discover the existence of simple relations. Thus, in the case of 11, what possible meaning can be attached to quantities obtained by subtracting the heat of formation of aqueous solutions of the haloid acids from that of

\* In this and the following case Thomsen inserts two other quantities which are multiples of the same constants, but they are in reality (as he shows) dependent on those given here.

I have not inserted the case of marsh-gas and carbon tetrachloride, the heat of formation of which is nearly the same; this is a constant of a different character and presents no difficulties.

the corresponding solid ammonium salt? This same case is also an instance of an entirely fictitious constant; from the fact that, in calculating the value of N, H<sub>4</sub>, Cl, the quantity H, Cl, aq. is involved, and also that the heat of neutralization of ammonia by the three haloid acids is identical, it follows, as Thomsen himself clearly shows, that each of the differences N, H<sub>4</sub>, Cl-H, Cl, aq. is made up of  $x-\Delta$ , where x is the same quantity in each case, and  $\Delta$  is the heat of dissolution of the ammonium salt concerned. So that the constancy depends entirely on the three values for  $\Delta$  being nearly equal (which we might well expect to be the case); these values are 3,880, 4,380, and 3,550 respectively, showing a variation of as much as 800 cal., which amounts to 20 per cent. of the whole, but, when imported into the large quantity of 36,000 cal., appears as little more than 2 per cent.

There are other points which must raise suspicion as to the reality of these constants. Why, for instance, amongst the many acids containing sulphur, should dithionic and tetrathionic acids alone show numerical relations? Why should  $P_2O_5$ ,  $As_2O_5$ , and  $As_2O_3$  form a group to the exclusion of  $P_2O_3$ ? Then, again, there may be found other quantities where there is as evident a numerical relationship as in many of those quoted by Thomsen, but in which this relationship is evidently accidental; thus, immediately opposite the page on

which No. 4 is given, we find

$$SO_2^{gas}$$
, aq. = 7,700,  
 $SO_2^{liq}$ , aq. = 1,500,  
 $SO_3^{liq}$ , aq. = 39,170;

which numbers may be expressed as

$$5 \times 1,540,$$
  
 $1 \times 1,500,$   
 $26 \times 1,507;$ 

although the difference between the first and second quantities is due to purely physical causes, and the other differences to chemical, or combined physical and chemical causes. Again, it may be observed that the numerical relations are in many cases scarcely of a very simple character, such fractions as  $\frac{3}{7}$ ,  $\frac{5}{14}$ , and  $\frac{8}{15}$  occurring; and, moreover, that the error is often of very considerable magnitude. Thus, in No. 12, P<sub>2</sub>, O<sub>5</sub> should be 386,650 cal., if the constant supposed to be shown in As<sub>2</sub>, O<sub>3</sub> is correct; whereas, if the constant given by P<sub>2</sub>, O<sub>5</sub> be correct, then As<sub>2</sub>, O<sub>3</sub> should be 147,960 cal., an error of either 16,750 or 6,710 cal. occurring; certainly out of all

proportion to the actual experimental errors: similar errors, amounting to 1,000 to 3,000 cal., could be mentioned in several of the other cases.

These last observations give, in fact, as I believe, the clue to an explanation of these supposed constants. By taking a sufficiently high fraction and allowing a sufficiently wide margin for "error," it is obviously possible to represent any two numbers whatever as multiples of the same constant. The whole question, therefore, resolves itself into one of

probabilities.

Thus in No. 1 the difference between the two quantities is 68,810 cal., and the error which the first of them shows as compared with the second is  $(111,590 - (3 \times 36,880) =) 1,150$ cal.; while the error which the second shows as compared with the first is  $(5 \times 37,197 - 184,400 =) 1,585$  cal., or a total error of 2,735 cal. is made allowable. Now it is obvious that if the error allowed had been as great as the difference between the two values (184,400 and 111,590), every quantity between these two numbers would have been regarded as thus related. As it is, however, only 2,735 out of 68,810, or 1 out of 25, numbers between these limits will show the relation; or, to put it in a more general form, of the numbers between 184,400 and zero, 1 out of 25 will be, within the given range of error, some submultiple by 5 of 184,400. Now, on examining the table (vol. ii. p. 401) which contains the data relating to the iodine compounds, we find 28 quantities less than 184,400, i.e. rather more than sufficient to give, through purely mathematical chances, the one case discovered by Thomsen.

With No. 2 there should be 74 numbers less than 72,970 cal. to give one coincidence within the limits assigned; there are, as a matter of fact, 49 such numbers amongst the nitrogen compounds (p. 406). With No. 3 there should be 28 numbers less than 300,080 amongst the phosphorus compounds to give the one coincidence, whereas we find there are really

24 such numbers.

With No. 4 it is certainly not legitimate to consider a quantity such as 192,920 to be a simple multiple of 103,240, when it can only be done by introducing the large fraction of  $\frac{1}{15}$  and a margin of 1,007 cal. as error. Taking, therefore, the numbers for S,O<sub>2</sub> and S,O<sub>3</sub> only, we find that there should be 74 numbers less than 103,240 to give the coincidence, whereas there are 35 such quantities amongst the data for sulphur.

Thus in these four cases there are two in which the data are nearly exactly as numerous as they should be if the coincidences were a matter of mere chance, whereas in the other two they are only  $\frac{3}{4}$  and  $\frac{1}{2}$  as numerous as they should be; but it must be remembered that we are only taking the actual data expressed in a limited number of ways, such as Thomsen happened to have selected, and that these same data might be expressed in numerous other ways, giving us a much longer list of numbers.

With Nos. 5 and 6, where the quantities are equal, the fallacy of their connexion may be well shown thus:—The two quantities in No. 5 are selected from the two pages (403, 404) on which the sulphur data exist: can we find numerical equality as striking by taking any other two pages of data? Taking p. 402, which contains iodine data, and p. 403, which

contains sulphur data, we find :-

$K, I, O_3$ (cryst. salt) = 1	24,490,
$S, O_3, H_2O$ (liquid acid) = 1	24,560,
$SO_3$ , aq. (heat of dissol. of solid $SO_3$ ) =	21,320,
I, $Cl_3$ (heat of form. of solid) =	21,490,
$SO_2$ aq., O (solution) =	63,630,
$\mathrm{HI}, \mathrm{O}_3 \; (\mathrm{anhydrous}) \; \ldots \; \ldots \; = \;$	64,000,
$S_2 O_7 H_2$ , aq. (heat of dissol.) =	54,320,
H, I, $O_3$ , aq. (heat of form. and dissol.) =	55,800.

Four instances of approximate numerical equality between quantities representing reactions which are altogether dissimilar.

Nos. 7, 8 and 9 refer to the formation of metallic compounds: they are the only ones of this nature quoted by Thomsen, and bear but a very small proportion indeed to the hundreds of values for metallic compounds given in vol. iii.\*

Of those cases which deal with differences between the heat of formation of similar compounds, Nos. 11 and 12 have already been discussed, and it is only necessary to point out further that these three instances form but a minute fraction of the

\* The heat of formation of the oxides of iron is partially dependent on that of the chlorides and on the heat of neutralization of the respective oxides by hydrochloric acid. It is possible that there is an error of 4,000 cal. or more in the determination of Fe<sub>2</sub>O<sub>3</sub>3H<sub>2</sub>O, 6HCl (vol. i. p. 410); since the difference between this quantity and the heat of neutralization of the same oxide by sulphuric acid is smaller by this amount than in any other known case. It is more probable, however, that the error is in the heat of neutralization by sulphuric acid, for the indirect determinations of it involved in the precipitation of iron sulphate by a barium salt (pp. 416, 417) give similarly anomalous numbers. Some recent determinations of these latter quantities (Fay, Chem. News, lvii. p. 36, and Pickering, ibid. lvii. p. 76) tend to show that this anomaly does not always exist with iron sulphate. It may have been due to the presence of colloidal ferric oxide in the solution.

almost infinite number of groups of compounds which might be constructed out of the 300 quantities given in Thomsen's 2nd volume. Similarly, also, the number of comparable reactions (Class C) which might be collected in the same field would certainly afford sufficient chances for the existence of the two coincidences shown in Nos. 13 and 14.

In the Berichte, v. p. 170, and vi. p. 239, Thomsen drew attention to the (supposed) existence of a common constant of affinity, of which the following are considered as proofs:—

$S, O_2$ $SO_2, O, aq.$ $*SO_4H_2, aq.$ $SO_2, O, H_2O$ . $*S, O_3, H_2O$ $*S, O_3, aq.$	$. = 4 \times 17,768$ $. = 4 \times 17,837$ $. = 1 \times 17,848$ $. = 3 \times 17,834$ $. = 7 \times 17,796$ $. = 8 \times 17,803$
~, ~ <sub>3</sub> , aq	
• • •	• • •
$N_2, O \dots$	$\cdot = 1 \times 18,316$
$N_2, O $	$. = 1 \times 18,300$
$N_2O_2$ , O, aq	$. = 2 \times 18,170$
$*N_2O_2, O_2, aq.$	$. = 3 \times 18,214$
$N_2O_2, O_3, aq.$	$. = 4 \times 18,235$
a 0 a0	0 10000
$Cu, O, SO_3, aq.$	$\cdot = 3 \times 18,070$
Pb, $O$ , $SO_3$ , aq.	$\cdot = 4 \times 18,888$
Fe, $O$ , $SO_3$ , aq.	$\cdot = 5 \times 18,772$
$Cd$ , $O$ , $SO_3$ , $aq$ .	$. = 3 \times 18,994$
$Zn$ , O, $SO_3$ , aq.	$. = 6 \times 18,077$
$Mg, O, SO_3, aq.$	$10 \times 18,092$
C= 2 0 00	_11 \ 12 052
$Cu, S, O_4, aq.$	$\cdot = 11 \times 18,058$
$Pb, S, O_4, aq.$	$=12 \times 18,163$
$Fe, S, O_4, aq.$	$\cdot = 13 \times 18,176$
$Cd, S, O_4, aq.$	$\cdot = 11 \times 17,882$
$Zn, S, O_4, aq.$	$\cdot = 14 \times 17,920$
$Mg, S, O_4, aq.$	$. = 18 \times 17,963$
$\mathrm{Br_2}\mathrm{aq.},\mathrm{H_2}$	$. = 3 \times 18,551$
$\operatorname{Cl}_2\operatorname{aq}_{\cdot},\operatorname{H}_2$ .	$. = 4 \times 18,441$
$H_2O_2$ aq., $H_2$ .	$. = 5 \times 18,335$

<sup>\*</sup> These are not fundamental quantities, but depend on the other accompanying quantities.

```
2\text{FeSO}_4 \text{ aq.}, 0, 80_3 \text{ aq.} . . . = 2 \times 18,400

2\text{CrO}_3 \text{ aq.}, 380_3 \text{ aq.} . . . = 2 \times 18,442

2\text{Mn}_2 \text{O}_7 \text{ aq.}, 280_3 \text{ aq.} . . . = 4 \times 18,162
```

 $\mathrm{Mn_2O_7}\,\mathrm{aq.}, 5\mathrm{H_2O_2}\,\mathrm{aq.}, 2\mathrm{SO_3}\,\mathrm{aq.}$  . =  $10\times18,924$   $\mathrm{Mn_2O_7}\,\mathrm{aq.}, 5\mathrm{H_2O_2}\,\mathrm{aq.}, 2\mathrm{H_2Cl_2}\,\mathrm{aq.}$  =  $10\times18,214$ 

The "perfect analogy" of these various reactions, even when we confine ourselves to the members of each separate group, is certainly of a somewhat questionable character, and, in my opinion, cannot be regarded as existing in even the most superficial sense; and where an analogy does exist, as in the formation of the six sulphates, we might expect the heat to be the same in every case, but can attach no meaning whatever to its being a multiple of some constant; nor can we understand why certain other perfectly analogous reactions should not exhibit a similar relationship if this constant had any true signification.

The variation, also, in this constant is somewhat large, amounting to 7 per cent. or  $x \times 1,226$ , where the value of x may be as high as 18, giving a maximum error of 22,068, a

quantity larger than the constant itself.

That this constant is of an entirely fictitious nature may be shown most palpably by taking any other number and tabulating all the thermal values which are multiples of it. The number 15,000 was taken in this way, and all the quantities which are multiples up to 10 of it, within an error of  $\pm 2.3$ per cent. only, are given in the accompanying table. They were selected from the data referring to the non-metallic and metallic combinations tabulated by Thomsen in vols. ii. and iii., and though they amount to nearly 120, they could no doubt be considerably increased by a more thorough and extended search. Out of these it is evident that we could form many tables of "analogous compounds," the heat of formation of which is some simple multiple of our "constant" 15,000, and a similar investigation would show that any number would act just as well as a "common constant of affinity."

The whole question, therefore, of these constants disappears, and resolves itself into the chances of coincidences occurring

in a certain number of numbers.

$C_2H_6, H_2$	14,940	CO, Cl <sub>2</sub>	$5 \times 15,296$
F. Cl. 4TI O	15 150	N: 012	
$\mathbf{FeCl_2}$ , $\mathbf{4H_2O}$		Ni, Cl <sub>2</sub>	$5 \times 14,906$
ZnBr <sub>2</sub> , aq.	15,030	SnCl <sub>2</sub> aq., Cl <sub>2</sub>	$5 \times 15,206$
Ni, H <sub>2</sub> Cl <sub>2</sub> aq	15,070	Pt, Cl., 2NaCl	$5 \times 14,744$
Pd(OH) <sub>2</sub> , 4HCl aq	14,930	SnCl <sub>2</sub> aq., Cl <sub>2</sub> Pt, Cl <sub>4</sub> , 2NaCl Tl <sub>2</sub> O, SC <sub>3</sub>	$5 \times 15,100$
Cu <sub>2</sub> O, 2HCl aq.	14,660	No O CO	5 15 194
O C STICIAL	15,000	Na <sub>2</sub> O, CO <sub>2</sub>	$5 \times 15,184$
CuO, 2HCl aq.	15,270		
CuO, 2HNO <sub>3</sub> aq Cu(OH) <sub>2</sub> , 2HCl aq	15,250	$N_2, H_4, O_3 \dots H_2 O_2 \text{ aq., } H_2 \dots $	$6 \times 14,677$
Cu(OH), 2HCl ag	14,910	HO ag H	$6 \times 15,236$
Cu(OH) <sub>2</sub> , 2HNO <sub>3</sub> aq	14,890	COL ATT	
C. D. D.	15 100	OOL:40	$6 \times 14,937$
$Cu_2Br_2$ , $Br_2$ , $NaOH$ aq., $HPH_2O_2$ aq.	15,190	S, O <sub>2</sub> , Cl <sub>2</sub> Bi, O, Cl, H <sub>2</sub> O	$6 \times 14,963$
NaOH aq., HPH <sub>2</sub> O <sub>2</sub> aq.	15,160	Bi. O. Cl. H.O	$6 \times 14,695$
NaOH aq., HC2HCl2O2	aq. 14,830	K, O, Cl, aq	$6 \times 14,669$
1, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2,		D; C1	6 15 105
$C_2H_4$ , $H_2$	$9 \times 15.345$	Bi, Cl <sub>3</sub> Sb, Cl <sub>3</sub>	$6 \times 15,105$
02114, 112	014.045	S0, C1 <sub>3</sub>	$6 \times 15,232$
C, O	$2 \times 14,045$	L1, Br, aq	$6 \times 15,218$
PCl <sub>3</sub> , Cl <sub>2</sub>	$2 \times 14,845$	$Na$ , $Br$ , $2H_2O$	$6 \times 15,048$
$N_2$ , $O_5$ , aq	$2 \times 14.910$	K, Br, aq	$6 \times 15,038$
Cl, O, H, aq	$2 \times 14.965$	7- D	
SoCI ag	2 × 15 195	Zn, Br <sub>2</sub> , aq	$6 \times 15,160$
SeCl <sub>4</sub> , aq	4 \ 10,100	$\operatorname{Cd}$ , $\operatorname{O}$ , $\operatorname{H}_2\operatorname{SO}_4$ , aq	$6 \times 14,980$
SnCl <sub>4</sub> , aq.	$2 \times 14,070$	$C$ , $O$ , $H_2SO_4$ , $aq$	$6 \times 14,678$
Tl, Cl	$2 \times 15{,}060$	Tl <sub>2</sub> O, 2HBr	$6 \times 15,303$
Ag, Cl	$2 \times 14.690$	Ag O 2HBr	$6 \times 15,163$
Hg O	$2 \times 15.335$	Ag <sub>2</sub> O, 2HBr Pt, Cl <sub>4</sub> , 2KCl	
$\mathrm{Hg}$ , $\mathrm{O}$ $\mathrm{Pd}$ , $\mathrm{O}_2$ , $\mathrm{2H}_2\mathrm{O}$	2 15 915		$6 \times 14,918$
Fu, O <sub>2</sub> , 211 <sub>2</sub> O	2 15,210		
$Hg_2O$ , $2HCl$ aq $2NaOH$ aq., $2PO_2H_3$ aq.	$2 \times 15,035$	P, Cl <sub>5</sub>	$7 \times 14,998$
2NaOH aq., 2PO <sub>2</sub> H <sub>3</sub> aq.	$2 \times 15,160$	Sb, Cl <sub>5</sub>	$7 \times 14,981$
2NaOH aq., H <sub>2</sub> SeO <sub>4</sub> aq.	$2 \times 15.195$	50,015	
	,	5, 0,	$7 \times 14,749$
TI O as	$3 \times 15,100$	S, O <sub>3</sub> Bi, O <sub>2</sub> , H, H <sub>2</sub> O	$7 \times 14,721$
H <sub>2</sub> , O <sub>2</sub> , aq		C, O <sub>2</sub> , aq K, Cl	$7 \times 14,691$
1 <sub>2</sub> , O <sub>5</sub>	$3 \times 15,010$	K. Ci	$7 \times 15,087$
NH <sub>3</sub> , HBr	$3 \times 15,007$	Na <sub>2</sub> , S, aq	$7 \times 14,857$
$C_2H_2$ , $H_2$ $Fe_2Cl_6$ aq., $Fe$	$3 \times 14,960$	G. G.	
Fe Cl ag Fe	$3 \times 14,803$	Sr, S, aq	$7 \times 15,241$
TI O H O	$3 \times 15,157$	$Mn, Br_2, aq$	$7 \times 15,160$
$\mathrm{Tl}_{2}^{2},\mathrm{O},\mathrm{H}_{2}\mathrm{O}$		$Z_n$ , O, $\tilde{H}_2SO_4$ , aq	$7 \times 15,157$
$\mathrm{Tl_2O}$ , $\mathrm{O_2}$ , $\mathrm{3H_2O}$	$3 \times 14,700$	Pb, N <sub>2</sub> , Õ <sub>6</sub>	$7 \times 15,066$
HgO, 2HCy	$3 \times 15{,}303$	2 0, 2 2, 0 g	.,,,
Pt, Cl <sub>2</sub> , 2KCl	$3 \times 15,063$		
		Sb, $O_2$ , $H$ , $H_2O$	$8 \times 14,736$
$\overrightarrow{\mathrm{CNH}}, 3\overrightarrow{\mathrm{H}}_2$	$4 \times 14,990$	K. I. O., aq	$8 \times 14,714$
		Li, Ó, H, aq	$8 \times 14,680$
Na, S, H, aq	$4 \times 15,125$	KNO	$8 \times 14,935$
$\mathbf{Zn}, \mathbf{I}_2, \mathbf{aq}.$ $\mathbf{Pt}, \mathbf{Br}_4, 2\mathbf{KBr}.$	$4 \times 15,137$	$K, N, O_3$	
Pt, Br <sub>4</sub> , 2KBr	$4 \times 14,815$	$\mathbf{M}_{2}, \mathbf{O}_{3}, \mathbf{SH}_{2}\mathbf{O}$	$8 \times 15,048$
Ni, O, H,O	$4 \times 15,210$	$P, O_2, H_3$	
	$4 \times 15,160$	P. O., H	$9 \times 15,296$
		Bi O 3H O	$9 \times 15,304$
$T_1, O, NO_2 \dots$	$4 \times 15,039$	Co. T. or	
		$\mathbf{Ca}, \mathbf{I}_2, \mathbf{aq}.$ $\mathbf{Na}_2, \mathbf{O}, \mathbf{H}_2\mathbf{O}.$	$9 \times 14,993$
P, Cl <sub>3</sub> P <sub>2</sub> , O, 3H <sub>2</sub> O	$5 \times 15,060$	Na <sub>2</sub> , O, H <sub>2</sub> O	$9 \times 15,042$
P. O. SH.O	$5 \times 14,972$	$K_2$ , O, $H_2$ O	$9 \times 15{,}320$
So O ag	$5 \times 15,332$		
			$10 \times 15,467$
N, H <sub>4</sub> Ul	$5 \times 15,158$		
	$5 \times 15,302$	$As_2$ , $O_3$ , $aq$	$10 \times 14,712$
CO, O, aq	$5 \times 14,768$	Sb, O <sub>3</sub> , H, H <sub>2</sub> O Mg, Cl <sub>2</sub> Ba, I <sub>2</sub> , 7H <sub>2</sub> O Sn, Cl <sub>4</sub> , 2KCl	$10 \times 14,857$
	$5 \times 14,784$	Mg, Cl.,	$10 \times 15,101$
	$5 \times 14,862$	Ba, I., 7H.O	$10 \times 15.137$
		Sn Cl 2KCl	10 × 15 141
	$5 \times 15,004$	M. O II O	10 × 14 000
Mn, I <sub>2</sub> , aq	$5 \times 15,140$	$Mg$ , $O$ , $H_2O$	$10 \times 14,896$
$\mathbf{Zn}, \mathbf{Br}_2$	$5 \times 15,186$	Ca, O, aq	$10 \times 14,926$
$\operatorname{Cd},\operatorname{Br}_2$	$5 \times 15,040$	Ca, O, aq Cd, O <sub>2</sub> , SO <sub>2</sub>	$10 \times 15,047$
Cd, Br <sub>2</sub> , aq	$5 \times 15,148$	Cd, O <sub>2</sub> , CO <sup>2</sup>	
- w, 2012, wq.,,,,,,,,,,,,	-,,20,220	, -2,	,

# VIII. Note on the Governing of Electromotors. By W. E. AYRTON and JOHN PERRY\*.

IN 1882 a method was brought forward by us for governing electromotors, so that their speed should not be varied by an alteration in the load. The method, which was worked out theoretically and experimentally, was based on the combination of a motor, which converted electric energy into mechanical energy, with a brake dynamo, which reconverted the surplus mechanical energy into electric energy. After passing through various stages the arrangement finally resolved itself into an electromotor having the field-magnet wound with a shunt- and a series-coil, the coils being so connected with the rest of the circuit that the currents passed round them in opposite directions. Hence the magnetic excitation of the field-magnet was produced by the difference in the number of ampere-turns of the two circuits passing round it.

This method of governing motors, which has since 1882 been reinvented in France by M. Deprez, in America by Mr. Sprague, and which has formed the subject of an exhaustive series of experiments carried out in Germany by Dr. Fröhlich, answers well and produces a very fair constancy of speed for very considerable variations of the load. But it has a very decided defect, arising from the fact that since the series- and shunt-coils on the field-magnet oppose one another's action, the magnetization cannot be produced as economically as if there were no such differential action. Mainly on this account we have not developed our method of governing as energetically as we might otherwise have

been led to do.

In our original investigation of the subject we considered the conditions for governing motors either when a constant PD. (potential-difference) or when a constant current was supplied, and in both cases the practical solution we arrived at was a differential winding of the field-magnet. But we have since noticed that, in the case of the supply conditions being constant current, our original equations could be differently interpreted, and that the demagnetizing series could be dispensed with. Consequently a motor for constant current can be made to go at a constant speed with a varying load, and in addition to have the high efficiency of a well-made dynamo.

We shall for the general consideration of the problem use the simplest equations for a motor, disregarding saturation,

<sup>\*</sup> Communicated by the Physical Society: read May 26, 1888.

as we did in our original paper, since, although the results so obtained for critical speed, &c., cannot be used directly without correction in actual practice, these equations are sufficiently accurate to show whether or not a certain combination is a possible or an impossible one for obtaining a certain required result.

If E be the back E.M.F. in the armature of a motor at a speed of n revolutions, if p be a term depending on the permanent magnetism in the iron of the field-magnet, S the current passing round the series-coil, and Z the current round the shunt-coil, we have

$$\mathbf{E} = n \left( p \pm q \, \mathbf{S} \pm t \mathbf{Z} \right). \quad . \quad . \quad . \quad (1)$$

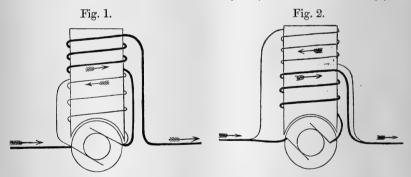
The signs + or — in the two terms being used as the seriesand the shunt-currents respectively help or oppose the permanent magnetism.

If s and z be the resistances of the series- and shunt-coils respectively, a the resistance of the armature, and A the current round the armature, we have in the case of what has been called a short shunt (fig. 1),

$$E = Zz - Aa$$
, . . . . . . (2)

and in the case of what has been called a long shunt (fig. 2),

$$E = Zz - A(a+s);$$
 . . . . (3)



and in both cases, if C be the constant current supplied to the motor,

$$C = A + Z$$
. . . . . . . . (4)

Now, remembering that in the case of a short shunt (fig. 1), C is equal to S, equations (1), (2), and (4) lead to

$$n \left\{ p \pm q \, C \pm t \, (C - A) \right\} = (C - A) z - Aa; \quad . \quad (5)$$

and in the case of a long shunt (fig. 2), remembering that C

is equal to A, equations (1), (3), and (4) lead to

$$n \left\{ p \pm q \, \mathbf{A} \pm t \, (\mathbf{C} - \mathbf{A}) \right\} = (\mathbf{C} - \mathbf{A})z - \mathbf{A} \, (a + s). \quad . \quad (6)$$

Equations 5 and 6 have then to be satisfied for all values of **A** for constant values of n and C; hence in the case of a short shunt,

 $\pm n (-tA) = -A (z+a), \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (7)$ 

and in the case of a long shunt

$$+n(q-t)A = -A(z+a+s)$$
. (8)

But t, q, z, a, and s are all positive quantities, and since t is always larger than q, that is the number of turns in the shunt-coil is always larger than the number of turns in the series-coil, it follows that to satisfy either equation (7) for the short shunt or equation (8) for the long shunt, the positive value of t in the original equation (1) can in either case alone be employed. In other words, whatever be the arrangement of the series-coil, the shunt-coil must be a magnetizing and

not a demagnetizing one.

This result we pointed out in our original paper on "Electromotors and their Government," in vol. xii. of the 'Journal of the Society of Telegraph Engineers and Electricians,' since on page 314 we stated that the solution for constant current was a shunt-motor with a series demagnetizing-coil; and it would be unnecessary to refer to this point again were it not that in one of the standard English treatises in which our method of governing motors is described in detail, the only solution for constant current that we are credited with is the impossible one of a series-motor with shunt demagnetizing-coil, the author not having observed that such a combination, whether used as a short or as a long shunt, could only make a motor run at a uniform speed when the speed was negative. Now, what does a negative value of n mean? It means that the armature must run the other way, or, in other words, that what was supposed to be a series-motor must in reality be the armature combined with a series demagnetizing-coil, that is must act as a series brakedynamo, and the supposed shunt demagnetizing-coil must, in conjunction with the armature, act as a shunt-motor; or, in other words, the solution is as we originally stated it-a shunt-motor with series demagnetizing-coil.

In another important English work our method is given correctly, but it is stated that the method would not work, because when a greater load was put on the motor the armature would go more slowly, the back E.M.F. would therefore be diminished, and less current would pass round

Phil. Mag. S. 5. Vol. 26. No. 158. July 1888.

the shunt-coil of the field-magnet. Hence the field-magnet would be weakened, which would cause the motor to go more slowly, and so on until it stopped and possibly reversed. This objection is a curious one, because exactly the same apparent difficulty might have been stated by the author of this treatise when he was dealing with our method of governing motors to run at a constant P.D. a few pages earlier. Here, however, he sees the explanation of the difficulty, and he points out quite correctly that, although it might at first sight appear anomalous to say that, in order to keep a motor running at a fixed speed, it is necessary to weaken the field of the motor when the load on it is increased, the explanation is found in the fact that the power depends not merely on the strength of the field but on the current passing through the armature, and that this latter is much increased when the field is weakened. Hence, on the whole, it is quite right to arrange matters so that the field is weakened when the load is increased. We say it is curious then, that while the author has explained the apparent difficulty so clearly when he was dealing with our method for governing motors when the supply condition was a constant P.D., he does not see that exactly the same explanation clears away the difficulty which he has himself raised regarding our method for governing motors to run when supplied with constant current.

What, however, we particularly wish to point out in this short note is that when the condition of supply is constant current it is not necessary to have a series demagnetizing-coil at all, and consequently the motor can be made to run at constant speed independently of the load, and in addition to

work with high efficiency.

We will first see whether such a solution is possible when the condition of supply is constant P.D. Let the motor be a simple shunt-motor; then, if as before E be the back E.M.F., n the speed, p a term depending on the permanent magnetism, and Z the current round the shunt,

$$E = n (p+tZ); . . . . . . (9)$$
  

$$E = Zz - Aa,$$

also

if z be the resistance of the shunt-coil, A the current in the armature, and a the resistance of the armature; also

$$V = \frac{Z}{z}$$

where V is the constant P.D. maintained at the terminal, of the motor;  $n\left(p + t\frac{V}{z}\right) = V - Aa.$  (10)

If n is to be constant as well as V, the left-hand side of the equation is constant, whereas the right-hand side varies with A the current through the armature, which must alter as the power given out by the motor alters. One solution for making this equation always true independent of the value of A is the well-known one of making a very small. When, however, a is not very small, and we have shown in detail elsewhere why we consider it a mistake to make the resistance of the armature as small in a motor as in a dynamo, equation (10) cannot be fulfilled for constant values of n and V, and a variable value of A; and in order that the equation may be made true a negative term proportional to A must be introduced on the left-hand side. The simplest way of doing this is to add a series demagnetizing-coil. Then (9) becomes

and (10) 
$$\mathbf{E} = n \ (p - q \ \mathbf{A} + t\mathbf{Z}),$$
$$n \left(p - q \ \mathbf{A} + t \frac{\mathbf{V}}{z}\right) = \mathbf{V} - \mathbf{A} \ (a + s),$$

an equation which will be always satisfied for any value of A if

$$n = \frac{a+s}{q}.$$

But when the supply is a constant current C supplied to the motor, the equation for a simple shunt-motor is

$$\mathbf{E} = n \ (p + t\mathbf{Z}),$$

$$\mathbf{E} = \mathbf{Z}z - \mathbf{A}a,$$

$$\mathbf{C} = \mathbf{A} + \mathbf{Z};$$

and, therefore,

$$n \{p+t(C-A)\} = (C-A)z-Aa.$$
 (11)

A now appears with a negative sign on both sides of the equation (11), and this equation will always be satisfied for any value of A if

$$n = \frac{z+a}{t}, \quad . \quad . \quad . \quad . \quad (12)$$

without there being any necessity for using a series demagnetizing-coil. At first sight, then, it appears as if an entirely new solution for governing a motor supplied with a constant current had been arrived at, consisting simply of using a shunt-motor. But on further examination it is seen that if we substitute in (11) the value given in (12) for n, we obtain for C the current for which the motor governs:

$$C = \frac{np}{z - nt}$$
$$= -\frac{np}{a}.$$

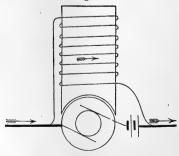
But as this is negative it is necessary, in order that the shuntmotor may govern, that the terminals of the motor should be reversed. This will reverse the current round the field-magnet; but, by hypothesis, not the residual magnetism, otherwise p would also become negative. The core of the electromagnet must, therefore, be of steel, so strongly magnetized that the shunt-current does not reverse the polarity, and the permanent magnet and rotating armature together form a brake-dynamo while the shunt-coil and the armature will form the motor. But this is simply one of the solutions (a theoretical one of course and not a practical one) given by us on page 310 of our original paper and illustrated in figure 10 on that page.

The fact, however, still remains that in the case of the supply condition being constant current, equation (11) can be satisfied without the employment of a series demagnetizing-coil; and all that we have to do to in order to make the solution a practical one, that is to enable an ordinary field-magnet with soft iron core to be employed, is to alter the equation so that when the speed equation (12) is satisfied (11) leads to a positive value of the current. This result may be obtained by adding to the right-hand side of equation (11) a positive constant term e numerically larger than np, for in that case, if

$$n = \frac{z+a}{t}$$

$$C = \frac{e-np}{a}$$

for all values of A. Now such a positive term e will be Fig. 3.



introduced on the right-hand side of equation e, if some accumulators of E.M.F. equal to e be introduced into the

armature circuit, as in fig. 3, the accumulators being joined up so as to help the main current C. In that case the resistance a of the armature must be increased by a', the resistance of the accumulators; and the two equations we are finally led to for the speed at which the motor governs, and the constant current for which it governs, are

$$n = \frac{z + a + a'}{t}, \quad . \quad . \quad . \quad . \quad (13)$$

$$C = \frac{e - np}{a + a'}. \qquad (14)$$

This solution is a practical one, and consists of a simple shunt-motor, with some accumulators in the armature circuit. Further, it is one not requiring many accumulators, for if np, the back E.M.F. of the motor due to the residual magnetism alone be small, as it will be if the field-magnet iron core be soft, and further, if a + a' be also not large, e need not be large in order that the value of C, the current for which the motor governs, may be as large as we like. The essence of this new method for making a motor supplied with a constant current revolve at a constant speed independently of the load does not consist in combining a shunt-motor with a series brake-dynamo, which was the essence of our original method, but in combining a shunt-motor with a store of electric energy in the armature-circuit, which store of energy, as the equations show, is automatically dealt out to help the motor exactly in proportion as the demand for power is required to keep the speed constant when the load on the motor is varied. And this store can be easily maintained by reversing the connexions of the accumulators when they are disconnected from the motor, and the motor is at rest, and leaving the accumulators without supervision to be charged by the constant current that is continuously supplied to the station.

While on the subject of electromotors it may be well to point out a fact which we thought was well known, viz. that when motors are being tested one against another for efficiency and for power developed per pound weight, it is most important that the motors should each be supplied with the P.D. they are intended to work at and should be run at their normal speed. But we have been much astonished to find in the 'Technology Quarterly' for September last, published by the Massachusetts Institute of Technology, a paper by Mr. H. Clifford on "The Efficiency of Small Electro-Motors," in which the results of experiments on the relative power and efficiency of a number of motors are given without any attention having been paid to the particular P.D. and

speed at which each motor was wound to work at. Mr. Clifford's results are arranged in tables which would be of considerable practical value were it not that the essential condition for making such tests has been absolutely disregarded. Hence Mr. Clifford's tables are not only valueless but are most misleading. We are able to speak definitely on the subject, because the results of the tests made on a motor of ours, which are quoted, are made with the motor running at less than half its normal speed, and supplied with less than one quarter of its normal power. As well might incandescent lamps intended to be run with very different P.Ds. be compared when run with totally wrong P.Ds., and a 100-volt lamp condemned as useless because when supplied with only 50 volts it emitted but little light.

IX. On the Formulæ of Bernoulli and of Haecker for the Lifting-power of Magnets. By Professor Silvanus P. Thompson\*.

RORMULÆ for the lifting-power of magnets have been given by D. Bernoulli and by Haecker, and more recently by Van der Willigen.

Bernoulli's empirical rule † is that the lifting-power varies as the cube root of the square of the magnet's weight, or

$$P \propto \sqrt[3]{W^2}$$

where P is the lifting power or pull exerted by the magnet in contact with its keeper, and W the mass of the magnet.

Haecker! gave precision to the rule by introducing a coefficient, the numerical value of which varies with the qualities of steel employed. Writing

 $P = a \sqrt[3]{W^2}$ 

he found that (when the unit of mass taken was the German pound) a had values between 8 and 10 for bar-magnets, and double these values for horseshoe-magnets. That is to say, according to Haecker a steel horseshoe-magnet weighing 1 pound could lift between 16 and 20 pounds, according to the quality of the steel and the intensity of its magnetization. The formula was found to be reasonably valid for magnets between  $\frac{1}{120}$  pound up to 40 pounds in weight.

Van der Willigen §, repeating the investigation partly with

\* Communicated by the Physical Society; read May 26, 1888.

† Acta Helvetica, iii. p. 233 (1758). † Pogg. Ann. lvii. p. 321 (1842).

<sup>§</sup> Sur le magnétisme des aimants artificiels, par V. S. M. Van der Willigen (Haarlem, 1878).

Haecker's own magnets and partly with more recent magnets made by Von Wetteren, by Elias, and by Logeman, found a somewhat different empirical rule. According to him the permanent lifting-power should be written

$$P = b \mathbb{K} \sqrt{A} \sqrt[4]{\frac{L}{\sqrt{A}}} \times \frac{L}{l};$$

where b is a constant depending on the quality of the steel and its degree of magnetization, K the perimeter of the polar surface, A the area of polar surface, L the length between the actual poles, and l the mean between interior and exterior lengths of the bar. For similar solids  $K\sqrt{A}$  is simply proportional to the surface A; so that this formula if applied to similar magnets merely means that the lifting-power varies as the polar surface, multiplied by a correcting factor which takes into account the proximity of the two poles. Van der Willigen found the coefficient b, which is virtually the same as Haecker's a, to vary, for good horseshoe-magnets, from 19·5 to 22·5.

If we consider the meaning of Bernoulli's and Haecker's formulæ, as applied to magnets of similar form, we shall see that the cube root of the square of the mass of the magnet is a quantity simply proportional to its polar surface, for the linear dimensions are proportional to the cube root of the mass, and the surface to the square of the linear dimensions. Hence, so far as similar forms of magnet are concerned, these rules mean nothing more or less than that the lifting-power is proportional to the polar surface. This we know from Joule's and many subsequent researches to be approximately true for magnets carried to equal intensity of magnetization.

Viewing the matter by the light of more recent researches on the induction of magnetism in closed circuits of iron or steel, we come to the same conclusion; for assuming that the magnetic induction B has been carried to an equal degree in the metal, the tension at any point in the circuit (in dynes per square centimetre) is\*

$$T = \frac{B^2}{8\pi},$$

and the element of the pull over area dA is

$$dP = TdA = \frac{1}{8\pi} B^2 dA;$$
$$P = \frac{1}{8\pi} \int B^2 dA,$$

whence

<sup>\*</sup> Maxwell's 'Electricity and Magnetism,' Art. 643.

which can be determined if the law of the distribution of the magnetic induction through the cross-section is known. Assuming this to be a simple uniform distribution (it is generally not quite so at the joint between the polar surfaces and armature of a magnet), this gives the pull (in dynes) as

$$P = \frac{1}{8\pi} B^2 A.$$

This formula\* affords a very convenient method of reckoning B from measurements made upon the pull exerted at a given polar surface; the formulæ becoming

B=5000
$$\sqrt{\frac{P \text{ kilos.}}{A \text{ sq. cm.}}}$$
;
B=1317 $\sqrt{\frac{P \text{ lbs.}}{A \text{ sq. in.}}}$ .

or

The a of Haecker's formula may, therefore, be taken as simply proportional to the square of the magnetic induction through the contact-surface, or

$$a = \frac{1}{8\pi} B^2 \cdot d^{\frac{3}{2}} \cdot c,$$

where d is the density of the steel, and c the ratio of the polar surface to the surface of one face of a cube of equal volume to that of the magnet.

Haecker found a for horseshoe-magnets twice as great as for bar-magnets. Van der Willigen found it from three to four times as great for horseshoes. Taking Haecker's figure, this shows that the long return-path through air of the tubes of magnetic induction offered so great a resistance that the steel magnet could only produce across the polar surface in

this case an induction  $\frac{1}{\sqrt{2}}$  times as great as when the closed horseshoe circuit was used.

Consideration of the rational formula will show that the greater lifting-power in proportion to their own weight possessed by small magnets, does not require for its explanation the sometimes alleged fact that small pieces of steel can be more highly magnetized than large pieces of steel. For, assuming equal intensity of magnetic induction, B, it is seen that the lifting-power is proportional to surface and not to weight; hence it must necessarily be greater relatively to weight in small magnets.

\* In Mr. Shelford Bidwell's paper, Proc. Roy. Soc. 1886, he uses a formula equivalent to  $\frac{1}{8\pi}(B^2-H^2)A$ , but without giving any reason for deducting H<sup>2</sup> from B<sup>2</sup>.

The net result of this paper is that Haecker's (and Bernoulli's) formula is merely another way of saying that the lifting-power of magnets in which the intensity of the magnetic induction has been carried up to an equal degree, is proportional to the polar surface. And Haecker's coefficient is proportional to B<sup>2</sup> through that surface.

### X. Notices respecting New Books.

Watts's Dictionary of Chemistry, revised and entirely rewritten By H. Foster Morley, M.A., D.Sc., and M. M. Pattison Muir, M.A., assisted by eminent Contributors. In Four Volumes. Vol. I. Longmans, Green, & Co., 1888.

THE standard work of reference in the English language used by chemists in this country and America is the well known 'Dictionary of Chemistry and the allied branches of other Sciences' bearing the name of the late Mr. Henry Watts as author. But this work was commenced more than a quarter of a century ago, and was only completed in 1881. During that period the rapid advancement of chemical science made it necessary to issue four supplementary volumes containing altogether between four and five thousand pages of additional matter. So rapid is the growth of the science, however, owing to the continuous increase in the number of workers, that an interval of seven years is sufficient to make even the last "Supplement" require further supplementing; and the late Mr. Watts had undertaken to revise the whole work and bring out a new and more condensed edition, representing the present state of chemical science, when his labours were cut short The lamented author had only gone so far as to prepare a code of "Instructions" for the use of contributors, and had written some sixty odd pages of the new edition at the time of his The completion of the work has been entrusted to Dr. H. Foster Morley and Mr. Pattison Muir, who have utilized Mr. Watts's materials as far as they go, but who have of course been obliged to supply the greater part of the matter which fills the pages of the present work.

The chief difference in form between the old edition and the new one, of which the first volume is before us, is the greater condensation which the publishers have insisted upon in the present issue. Instead of the nine thick volumes which chemists have been so long in the habit of consulting, the new edition is to be compressed into four volumes of about 750 pages each. Whether this condensation can be effected without serious injury to the Dictionary will depend entirely upon the skill and judgment which the compilers exercise in carrying on the work: it must be confessed that as far as the present volume is concerned there is no complaint to be made on this score. The 752 pages of the first volume are as replete with well organized information as could be desired by the most rapid of readers. There can be no doubt that much of

the older edition was unnecessarily lengthy and that many of the articles were out of place in a dictionary of pure chemistry, so that there has here been ample scope for condensation. On the other hand, when we consider that the subject of organic chemistry as treated in Beilstein's *Handbuch*, the most perfect type of compressed information at present at the disposal of chemists, requires three large volumes of the most closely printed matter, it is difficult to see how the compilers are going to treat of the whole of the science in the prescribed limits. But we must not anticipate difficulties since the present notice refers only to the first volume, and in this Messrs. Morley and Muir have certainly shown their ability to perform the literary feat which has been demanded of them.

The first volume of the Dictionary, which we are glad to see is still to retain the name of the late author of the first edition, takes us as far as the letter C, the concluding article being on Chemical Action. The work of editing has been facilitated by each editor taking charge of one of the two great divisions of the science, Mr. Muir being responsible for the inorganic and general chemistry, and Dr. Morley for the organic portion of the subject. This division of labour was no doubt necessitated by purely practical considerations, since the unavoidable tendency to specialization among modern workers has arisen from the enormous multiplication of facts, which renders it more and more hopeless for a chemist to become an adept in both departments of his science in the present state of its development. While conceding the practical necessity for this division of our science into organic and inorganic, we only do so with the understanding that there are not two chemistries, but that the compounds of the one particular element carbon, having been studied in greater detail than those of any other element, and the number of these compounds being practically unlimited, the mere wealth of material in this department of knowledge claims all the faculties of the chemist who devotes himself to its This multiplicity of carbon compounds is of course nothing more than an accident contingent upon the nature of the atom of the element on the one hand and of our present methods of investigation on the other. With the development of the science and the consequent perfection of our methods of research, we may expect to see the chemical histories of other elements developed into a state of complexity comparable with that of carbon, and the "organic" chemist of the future may be rivalled as a specialist by his brother worker on the compounds, say, of silicon, or of any other element to which new methods of investigation may be applied.

Among the features of the new edition to which attention must be called are the special articles contributed by various writers, many of whom are recognized authorities on the subjects of which they treat. Nineteen such contributors, including the late Mr. Watts, figure in the present volume. Taking these in the order given in the list at the commencement of the work, we have articles on Cellulose by Mr. C. F. Cross, on Analysis by Prof. Dittmar, on Diazo-Compounds by Mr. A. G. Green, on Chemical Change by Dr. J. Hood, on Blood by Dr. Halliburton, on Benzil and allied subjects by Dr. Japp, on Bacteria by Prof. Ray Lankester, on Allotropy by Prof. Lothar Meyer, on Azo-Colouring Matters by Prof. Meldola, on Affinity by Prof. Ostwald, on Amylamines by Dr. Plimpton, on Acids and Alloys by Prof. Ramsay, on Arabic acid &c. by Mr. C. O'Sullivan, on the detection and estimation of Poisonous Alkaloids by Dr. Stevenson, on States of Aggregation by Prof. J. J. Thomson, on Atmosphere by Prof. T. E. Thorpe, on the Ash of Organic bodies by Mr. Warington, and on Caoutchouc by Mr. C. J. Wilson. A portion of the article on Alcohols and many

minor articles are by the late Mr. Watts. It would be invidious to make any lengthy comments on these special articles, but we cannot refrain from expressing satisfaction at the co-operation of Continental chemists which the editors have We allude more especially to the valuable contributions of Profs. Ostwald and Lothar Meyer. The article on Bacteria by Prof. Lankester is an interesting example of the encroachment of Biology into the domain of Chemistry, and serves well to illustrate the mutual advantage arising from the contact of different branches of science. The same principle is seen with respect to Chemistry and Physics in the articles on Allotropy, Affinity, and States of Aggregation; but the interdependence of these two branches of science is too well known to need insisting upon here. Perhaps one of the most remarkable signs of the activity of research in a special group of products is seen in the articles on Azo- and Diazo-Compounds, which together fill over 36 pages. Some lengthy articles which fully merit the title of "special" are written by the editors, such for instance as Mr. Muir's very useful contribution on "Atomic and Molecular Weights," which covers about 25 pages.

One important difference between the present and the older edition is the printing of the pages in double columns, an innovation in which we must confess we fail to see any advantage from the reader's point of view. Another innovation is the use of large thick capitals for the words heading each article, and this is a decided improvement, as on running down the columns the eye at once catches the heading sought. Whilst on the subject of print we should like to express dissent from the plan of inserting hyphens into the names of compounds with the lavish profusion which the editors have adopted. Opening the volume at random we find such words as "Tetra-amido-iso-di-naphthyl" (p. 169), "wa-Dibromo-wo-di-nitro-ethyl-benzene" (p. 591), and so on throughout. Our chemical names are surely sufficiently long as it is without spreading them out into what an American humourist calls an alphabetical panorama. We fully admit that the subject of chemical nomenclature is a very difficult one to deal with in a thoroughly systematic manner, and we protest equally against the Continental custom of fusing up all the component syllables into one immense word. Thus in the number of the *Berichte* just to hand we find a paper on the condensation of "Tetramethylphenylamidocrotonsäureester." In the present state of nomenclature some compromise between these two extremes seems the most

practicable way of dealing with complex names.

The relative complexity of the two main divisions of Chemistry is well seen in the introductory explanations which each editor contributes to his own branch. Mr. Muir finds less than a page sufficient to enable those who consult the Dictionary to understand the plan of the articles on Inorganic and general Chemistry, while Dr. Morley has had to contribute an introduction to the articles on Organic Chemistry of seven pages in length. This last introduction is based on the code of instructions drawn up by the late Mr. Watts for the use of the abstractors for the Chemical Society's Journal, and will be found of the greatest use, nay, absolutely indispensable before the scheme of the organic portion of the work can become thoroughly familiar to those who use it for reference. The plan laid down in these instructions has been fairly well adhered to; but we must express regret that Dr. Morley has not made use of his present opportunity of helping to some extent the systematizing of our nomenclature by entirely sweeping away such trivial names as resorcin, pyrocatechin, and hydroquinone, which are all distinctly phenolic substances.

In concluding this notice we have only to congratulate English chemists on this distinctly valuable addition to their literature, and to express satisfaction at the manner in which the editors have performed their task in the completion of the first instalment of what must necessarily be a very onerous undertaking. It is to be hoped that the succeeding volumes will be brought out with all possible speed, for at the present rate of discovery in chemical science the first volume of a big dictionary may be almost out of date before the last volume appears, if too long an interval is allowed to elapse. We may add that Technological Chemistry finds no place in the present work, as this branch of the subject is to form a

separate treatise now being edited by Prof. Thorpe.

A Treatise on Alcohol, with Tables of Spirit Gravities. By THOMAS STEVENSON, M.D. Second edition. London: Gurney and Jackson. 1888.

The set of tables contained in this small volume of 73 pages have been compiled from the most trustworthy sources; and it is interesting to find that, after a searching examination into all the determinations of specific gravities by previous experimenters, the author gives the preference to the early experiments of Blagden and Gilpin, carried out in the last century (Phil. Trans. 1790, 1792, and 1794). Of these results he says:—"The accuracy and fidelity with which the work was executed, and the refinement of the methods employed, have called forth the warmest admiration and praise from those who have taken the pains to examine their work, which would do honour to the more refined science of our day.

Fownes's experiments, made more than half a century later, are not for one moment to be compared as to accuracy with the earlier experiments of Gilpin." Dr. Stevenson's tables give the sp. gr. to four decimal places at 60° F. (water at 60° F. = 1), the percentage of alcohol by weight and by volume, and the percentage of proof spirit. The little book must in future be at the right hand of all analysts who have to do with spirit determinations.

### XI. Intelligence and Miscellaneous Articles.

ON THE VELOCITY OF THE PROPAGATION OF SOUND. BY MM. J. VIOLLE AND TH. VAUTIER.

IN a previous communication the authors described the methods by which they were enabled to follow for several minutes the propagation of a wave in the interior of a cylindrical pipe 0.7 m. in diameter. The following are the principal results of this research.

The experiments with the pistol are summed up in the following table, which gives for different charges the time taken by the front

of the wave to travel once, twice, ... n times the path 2L.

Charges of the pistol.		Duration of t	he course 2L.	
the pistol.	$t_1$ .	$t_2$	$t_3$ .	$t_4$ .
gr.	S	S	8	8
3	37.257	37.334	37.384	37.420
2	•262	•348	•392	,,
1	.279	•350	•408	,,

It follows undoubtedly from these numbers that the velocity of the propagation of the wave diminishes with the intensity.

We shall put therefore t - A - B

$$t = \mathbf{A} - \mathbf{B} \sqrt{\mathfrak{Y}_{j}};$$

A and B being two constants to be determined, and  $\mathfrak{P}_j$  the mean pressure during the jth course, which pressure is given by our manometric measurements.

Taking A=37<sup>s</sup>·460 and B=0·69, the pressures being measured in millimetres of water, we have:—

Charges of the pistol.	Duration calculated.			
the pistol.	$t_1$ .	$t_2$ .	$t_3$ .	$t_4$ .
gr.	8	S	S	s
gr. 3	37.244	37.335	37.388	37.418
2	.262	•346	•344	• • • • • • • • • • • • • • • • • • • •
1	•280	•356	•400	"

A representing the duration of the course 2L for an infinitely small condensation,  $\frac{2L}{A}$  is the velocity of propagation of an infinitely small wave under the conditions of the experiment.

From this we easily deduce the limiting velocity to zero, and in dry air in the interior of the pipe in question, and therefore

the velocity in free air. The number thus obtained, 331·2 metres, is a little higher than that of Regnault, but is near that obtained more than sixty years ago by the members of the Bureau des Longitudes.

By numerous experiments made with different instruments (foghorn, organ-pipes, &c.), we have ascertained that the height of the sound has no influence on the velocity of propagation of the wave.

We have found, in fact, for the time of propagation of the wave

along the first path 2L:-

		sec.
$ut_{-1}$	Bombardon	37.30
$ut_{-1}$	Flute	$\cdot 42$
ut,	Flute	•38
ut.	Flute	•40
fa a	Double Bass	•37
fa,	Horn	•38
Sib	Cornet	•38
	Cornet	

The small differences observed seem to be due merely to differences in the intensity of the wave in the various cases.

The movement of the wave is independent of the vibrations which it carries along.—Comptes Rendus, April 3, 1888.

# ON THE ELECTRIFICATION OF METAL PLATES BY IRRADIATION WITH ELECTRICAL LIGHT. BY WILLIAM HALLWACHS.

At the close of an article recently published \* I had mentioned that, to judge from preliminary experiments, metal plates become electrostatically charged when irradiated with the electrical light. It could be seen from the outset that we were not dealing here with charges at potentials that could be measured by a goldleaf electroscope. In order to ascertain whether a charge measurable with sensitive electrometers could not be obtained, the final experiments were made as follows:- The circular metal plate, 8 centim. in diameter, to be illuminated was suspended by an insulated wire in the centre of a cylindrical sheet-iron vessel, 50 centim. in length and 37 centim. in diameter, which lay with its axis horizontal. The surface of the metal plate was coated with rust, but one portion of the surface was brightly polished and was put to earth. The wire by which the plate was suspended passed through, but insulated from, an earth-connected brass tube, to a Hankel's electrometer, which was chosen for these experiments on account of its small capacity. In the lid of the metal cylinder was a circular aperture of about 8 centim. diameter, which transmitted the rays of the arc lamp to the plate hanging inside. This aperture was covered by a piece of wire gauze, in order to prevent any appreciable induction of the lamp on the plate to be

<sup>\*</sup> Wiedemann's Annalen, vol. xxxiii. p. 301.

irradiated, without excluding the action of the luminous rays on it. From former experiments\* this latter phenomenon was to be expected, and was confirmed by the present experiments. The luminous arc was at a distance of 45 centim. from the plate, the rays coming from it passed through a diaphragm 6 centim. in

diameter before entering the metal case.

The case was of rusty iron, so that the contact potential against the plates to be suspended was always negative. In this case only could the rises of potential indicated by the electrometer be indubitably explained. For if the plate had been negative to the case, a rise of potential would have occurred due to the transport of negative electricity by the illumination. If the plate, however, was positive towards the case, and therefore possessed a positive charge, an increase of potential could only be due to the fact that positive electricity was produced on the plate by irradiation. The determination of a difference of potential due to contact by a method formerly described†, gave for rusty iron towards brightly polished zinc 1·2 volts.

If, now, the aperture in the diaphragm through which the rays of light could fall on the plate was closed by a mica plate, the electrometer was at rest when the arc was produced. When the mica was replaced by a far thicker plate of selenite, the galvanometer gave a gradually increasing deflection indicating positive electricity. This at once ceased to increase when the mica again replaced the selenite. The rise of potential cannot therefore be due to an inductive action, nor can it be referred to the action of heat. The complete absorption of the action by mica, and the great transmissibility of selenite are here as prominent as in the action of light on electrostatically charged bodies, so that the excitation of electricity is probably due to the same rays as that phenomenon.

The metals which have been used for the experiments just described were zinc, brass, and aluminium. In all three positive electricity occurred on irradiation with brightly polished surfaces. Old surfaces no longer show the phenomenon. The radiation itself lowers the potential to which the plates can be electrified, so that with any succeeding experiment made with the same surface, the potential obtained is lower, while the rise to it takes place more rapidly, and the decrease is greater than when for the same interval of time between the experiments the plate was not illumined. The maximum potential with zinc amounts to over a volt, with brass to about one volt, and with aluminium to 0.5 volt. These values are the highest which have as yet been obtained, as the maximum values change with the condition of the surface.

As I have had to interrupt these experiments, I have ventured meanwhile to communicate the chief results. Whether the excitation of electricity by radiation with electric light is in direct connexion with the loss of electricity by electrostatically charged

<sup>\*</sup> Loc. cit. p. 305.

<sup>†</sup> Wiedemann's Annalen, vol. xxix. p. 7 (1886).

bodies when irradiated, I cannot state, as it has hitherto been impossible for me to make any experiments in this direction.— Göttinger Nachrichten, May 1888.

#### THE BENECKE PRIZE IN PHILOSOPHY.

The Philosophical Faculty of the University of Göttingen pro-

pounds the following as the subject for the year 1891:—

In the last decades the fundamental importance of the law of entropy for the theory of all those physical and chemical phenomena, which are attended with a production or absorption of heat, has acquired greater prominence. And more especially in those essays on the law of energy which competed for the Benecke prize in 1884, has it appeared that the law of entropy is necessary for the completion of the law of energy. Simultaneously with this, the researches which have had for their object the establishment of the law of entropy on the basis of general mechanical principles, have in recent times made important progress. A comprehensive treatment of all questions which are connected with the law of entropy appears therefore particularly desirable at the present time.

Such a treatment should in the first place give the development of the law of entropy, in connexion with a thorough restatement and justification of Carnot's researches; it would then have to discuss, not only historically but also critically, the investigations in reference to the connexion of the law of entropy with the general principles of mechanics; it should finally contain a comprehensive report on all the applications which the law of energy has found in

the theory of physical and chemical processes.

The essays are to be sent in to the Philosophical Faculty of Göttingen not later than the 31st August, 1890. They may be written either in German, Latin, French, or English, and must be accompanied by a sealed letter containing the name, profession, and address of the author, and which on the outside must have a motto the same as that on the competitive essay.

The prizes will be awarded on the 11th of March, 1891, the birthday of the founder, at a public session of the Philosophical

Faculty.

The first prize is 1700 marks (£85), and the second 680 marks

(£34).

The memoirs to which prizes are awarded remain the unrestricted

property of the authors.

The titlepage of any competitive essay must also state the address to which the paper is to be returned in ease it is not found worthy of a prize.

The subject of the prize which is to be competed for to the 31st August, 1889, is to be found in No. 5 of the Göttinger Nachrichten

for the year 1887.

# LONDON, EDINBURGH, AND DUBLIN

# PHILOSOPHICAL MAGAZINE

AND

# JOURNAL OF SCIENCE.

# [FIFTH SERIES.]

#### A U G U S T 1888.

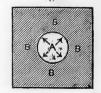
XII. The Function of Osmotic Pressure in the Analogy between Solutions and Gases. By Professor J. Van't Hoff\*.

DURING an investigation which required some knowledge of the laws regulating chemical equilibrium in solutions, the conclusion has gradually been evolved that a deep analogy—indeed almost an identity—exists between dilute solutions exerting osmotic pressure on the one hand, and gases under ordinary atmospheric pressure on the other. The following pages contain an attempt to explain this analogy; and the physical properties of such systems will form the first subject of discussion.

I. Osmotic Pressure—the nature of the Analogy due to this conception.

In order clearly to realize the quantity referred to as osmotic pressure, imagine a vessel, A (fig. 1), comFig. 1.

pressure, imagine a vessel, A (fig. 1), completely full of an aqueous solution of sugar, placed in water, B. If it be conceived that the solid walls of this vessel are permeable to water, but impermeable to the dissolved sugar, then, owing to the attraction of the solution for water, water will enter the vessel A up to a certain limit, thereby in-



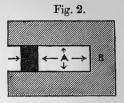
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creasing the pressure on the walls of the vessel. Equilibrium then ensues, owing to the pressure resisting further entry of water. This pressure we have termed osmotic pressure.

Phil. Mag. S. 5. Vol. 26. No. 159. Aug. 1888.

<sup>\*</sup> Communicated to the Physical Society; translated by Prof. W. Ramsay, F.R.S.: read June 9, 1888.

It is evident that this state of equilibrium might have been attained in A without entry of water if the vessel had been constructed with a piston, compressing the solution with a pressure equal to the osmotic pressure (fig. 2). It follows moreover



that, by increasing or diminishing the pressure on the piston, the state of concentration of the liquid can also be altered, owing to the passage of water through the walls of the vessel

in an outward or inward direction.

Such osmotic pressure has been experimentally investigated by Pfeffer (Osmotische Untersuchungen, Leipsig, 1887). walls of the cell consisted of unglazed porcelain, rendered impermeable to sugar though not to water, by filling it with a solution of potassium ferrocyanide and placing it in a solution of copper sulphate. Owing to diffusion, the ferrocyanide and the copper-salt come in contact after some time, and produce a membrane of copper ferrocyanide having the required properties. Such a vessel is then filled with a one-per-cent. solution of sugar; it is then closed with a cork provided with a manometer, and sunk in water; the osmotic pressure gradually rises, owing to entry of water, and the pressure due to the entry of water is read off when it becomes constant. an example of the results obtained, it may be mentioned that a one-per-cent. solution of sugar (which, owing to its considerable mass, was not appreciably diluted on entry of water) exerted at 6°.8 a pressure of 50.5 millim. of mercury—about one fifteenth of an atmosphere.

The porous membrane, such as that described, will be termed in the following pages a "semipermeable membrane;" and the conception will be made use of even where experimental verification is lacking. The behaviour of solutions may thus be studied in a manner strikingly analogous to that employed in the study of gases, inasmuch as what is known as "osmotic pressure" corresponds to pressure, or, as it is commonly but incorrectly termed, "tension" of a gas. It is right to mention that this is no fanciful analogy, but a fundamental one; the mechanism which, according to our present views, controls the pressure of gases and the osmotic pressure of liquids is substantially the same. In the former case pressure is due to the impacts of gaseous molecules on the walls of the containing vessel, and in the latter to the impacts of the molecules of the dissolved substance on the semipermeable membrane, since the impacts of the molecules of the solvent, being equal and opposed on each side of the vessel, may be neglected.

The great practical advantage arising from this method of regarding the behaviour of solutions, which leads at once to quantitative conclusions, consists in the fact that the application of the second law of thermodynamics to liquids is rendered exceedingly easy; for reversible processes, of which this law treats, can now be very simply conceived. It has already been mentioned that a piston and cylinder with semipermeable walls, placed in the solvent, permits of alteration of concentration of the solution contained therein, by alteration of the pressure on the piston, in exactly the same way as a gas can be rarefied or compressed; except that in the former case it is the solvent which escapes through the semipermeable walls on increase of pressure. Processes of this kind can always be made reversible, if care be taken that the pressure on the piston is made equal to the opposed pressure, that is, in the case of solutions, the osmotic pressure.

We shall make use of this practical advantage in the following pages, particularly in investigating the laws of "ideal solutions;" that is to say, solutions so dilute as to be comparable with "ideal" or "perfect" gases, in which the action on one another of the dissolved molecules, as well as their actual volume compared with that of the space they inhabit,

is so small as to be negligible.

## II. Boyle's Law for Dilute Solutions.

The analogy between dilute solutions and gases acquires at once a quantitative form, if it be noted that in both cases alteration of concentration exercises a similar influence on pressure, and is in both cases proportional to the pressure.

This proportionality, which for gases goes by the name of Boyle's law, may be proved experimentally for liquids, as well

as deduced theoretically.

Experimental Proof (Determination of osmotic pressure for solutions of various concentrations).—Let us first adduce Pfeffer's determinations (Osmotische Untersuchungen, p. 71) of the osmotic pressure (P) in sugar-solutions at the same temperature (13°·2 to 16°·1), and with varying concentrations (C):—

C.	P.	$\frac{\mathbf{P}}{\mathbf{C}}$ .
1 per cent.	535 millim.	535
2 ,,	1016 "	508
2.74 ,,	1518 "	554
4 ,,	2082 ,,	521
6 ,,	3075 ,,	513
	G 2	

The approximately constant quotients  $\frac{\mathbf{P}}{\mathbf{C}}$  point conclusively

to this proportionality between pressure and concentration.

Comparison of Osmotic Pressures by Physiological Methods. -Observations of de Vries ("Eine Methode zur Analyse der Turgorkraft," Pringsheim's Jahrb. xiv.) show that equal changes of concentration of solutions of sugar, and of potassium sulphate and nitrate, exercise equal influence on the osmotic pressure. This osmotic pressure was compared, by physiological methods, with that of the contents of a plantcell; the protoplasmal envelope contracts when it is immersed in solutions possessing great attraction for water. By a systematic comparison of the three bodies mentioned, using the same cells, three isotonic liquids (i. e. liquids exhibiting the same osmotic pressure) were obtained. Cells of a different plant were then made use of, and so four isotonic series were constructed which showed a similar proportion in their concentrations: this is exhibited in the following table, where the concentrations are expressed in gram-molecules per litre :--

Series.	KNO <sub>3</sub> .	$C_{12}H_{22}O_{11}$ .	$K_2SO_4$ .	$KNO_3 = 1$ .	$C_{12}H_{22}O_{11}$ .	K <sub>2</sub> SO <sub>4</sub> .
I	0.12	_	0.09	1		0.75
II	0.13	0.5	0.1	1	1.54	0.77
III	0.195	0.3	0.15	1	1.54	0.77
IV	0.26	0.4		1	1.54	

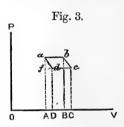
Theoretical Proof.—These observations render highly probable the existence of proportionality between osmotic pressure and concentration, and the theorem may be completed by a theoretical proof which is, indeed, almost selfevident. Regarding osmotic pressure as due to a kinetic cause (i. e. as produced by impacts of the dissolved molecules), there must exist a proportionality between the number of impacts in unit time and the number of molecules in unit volume. The proof is therefore exactly the same as that for Boyle's law. If, on the other hand, osmotic pressure be regarded as the outcome of an attraction for water-molecules, its value is evidently proportional to the number of attracting molecules in unit volume, provided (and this is taken for granted in sufficiently dilute solutions) the dissolved molecules exercise no attraction on each other, and each one exerts its own special attractive action, uninfluenced by its neighbours.

## III. Gay-Lussac's Law for Dilute Solutions.

While the proportionality between concentration and osmotic pressure is self-evident, so long as temperature remains constant, the proportionality between osmotic pressure and absolute temperature, the concentration being maintained constant, is not so manifest. Yet proof can be furnished from thermodynamical considerations; and experimental data exist which are highly favourable to the results predicted on thermodynamical grounds.

Theoretical Proof.—It has been already mentioned that, by means of a piston and a cylinder with semipermeable walls, reversible processes can be conceived to occur. If such processes are expressed in the way common as regards gases, volume and pressures are indicated on the lines O V and O P

(fig. 3); but pressure in this case, as before, must be taken as osmotic pressure. The initial volume (V cub. metres) is represented by OA; the initial pressure on the piston of area 1 square metre (P kilogr.) by Aa; and the absolute temperature by T; the solution is then conceived to undergo a minute increase of volume,



dV cubic metres (=AB), by moving the piston through dVmetres, while the temperature of the solution is maintained constant by introduction of the requisite amount of heat. amount of heat can be at once determined, inasmuch as it is equivalent to the external work performed, PdV, by the motion of the piston. Internal work is absent, for the dilution is, by hypothesis, so great that the dissolved molecules exercise no attraction on each other. This isothermal change ab is succeeded by the isentropic or adiabatic change bc, during which heat is neither absorbed nor evolved; the temperature sinks by dT°; and the original condition is then brought about by a second isothermal and a second adiabatic change, cd and da, respectively. The second law of thermodynamics requires that the fraction,  $\frac{d\mathbf{T}}{\mathbf{T}} \mathbf{P} d\mathbf{V}$  of the initially imparted heat charge PdV shall have been converted into work; this must be equivalent to the area abcd; and hence the equation follows:  $\frac{d\mathbf{T}}{\mathbf{T}} \mathbf{P} d\mathbf{V} = a b c d = af \cdot \mathbf{AB} = af d\mathbf{V}$ ; and hence  $P \frac{dT}{T} = af$ . But af represents the change of osmotic pressure, volume being kept constant, due to the change of temperature dT; i. e.  $\left(\frac{dP}{dT}\right)_{V}dT$ ; hence

$$\left(\frac{d\mathbf{P}}{d\mathbf{T}}\right)_{\mathbf{v}} = \frac{\mathbf{P}}{\mathbf{T}}$$

On integration this equation gives, on the assumption of constant volume,

 $\frac{P}{T}$  = constant;

that is, the osmotic pressure is proportional to the absolute temperature, provided concentration (which is here equivalent to the volume of a gas) remain constant; and this is entirely in accordance with Gay-Lussac's law connecting the

pressure and temperature of gases.

Experimental Proof (Determination of the osmotic pressure at different temperatures).—Let us compare this theoretical conclusion with the experimental data furnished by Pfeffer (pp. 114-115). He found that the osmotic pressure increases with rise of temperature; it will be seen that, although his results do not furnish a conclusive proof of the correctness of the theorem, yet there is a most striking correspondence between experiment and theory. If we calculate from one of two experiments at different temperatures the osmotic pressure to be expected in the other, by help of Gay-Lussac's law, and compare it with the experimental result, we have the following series:—

1. Solution of cane-sugar. Pressure at 32°, found 544 millim. Pressure at 14°·15, calculated. 512 found 2. Solution of cane-sugar. Pressure at 36°, found 99 Pressure at 15°.5, calculated 520.5 found 3. Solution of sodium tartrate. Pressure at 36°.6, found Pressure at 13°.3, calculated found . 1431.6 4. Solution of sodium tartrate. Pressure at 37°.3, found Pressure at 13°·3, calculated " found 908 "

Comparison of the Osmotic Pressure by Physiological Methods.—In the same manner that support has been lent to the application of Boyle's law to solutions (viz. that different substances in isotonic solutions retain their equality of osmotic pressure so long as their respective concentrations are reduced to the same fraction), so the application of Gay-Lussac's law receives support by the fact that this isotonic

state is maintained during equal alterations of temperature. It has been proved by physiological methods by Donders and Hamburger (Onderzoekingen gedaan in het physiologisch. Laboratorium der Utrechtsche Hoogeschool [3] ix. p 26), making use of blood-corpuscles, that solutions of potassium nitrate, sodium chloride, and sugar, which at 0° are isotonic with the contents of these cells, and hence are isotonic with each other, exhibit the same isotonic state at 34°; this is seen in the annexed table:—

Experimental Proof of Boyle's and Gay-Lussac's Laws for Solutions. Experiments by Soret (Archives des Sciences phys. et nat. [3] ii. p. 48; Ann. Chim. Phys. [5] xxii. p. 293).— The phenomenon observed by Soret lends a strong support to the analogy between dilute solutions and gases in respect of the influence of concentration and temperature on pressure. His work shows that just as in gases the warmest part is the most rarefied, so with solutions the warmest portions are the most dilute; but that in the latter case a much longer time must be allowed for the attainment of equilibrium. The experimental apparatus consisted of a vertical tube, the upper portion of which was heated while the lower portion was kept at a low temperature.

Soret's latest experiments lend a quantitative support to our analogy. As with gases, it is to be expected that when the isotonic state is produced, the solution will exist in equilibrium; and as the osmotic pressure is proportional to concentration and to absolute temperature, the isotonic state of different portions of the solution will occur when the product of the two (absolute temperature and concentration) are equal. If we therefore calculate, on this basis, the concentration of the warmer part of the solution from data obtained with the colder, the values compare with those

found as follows:-

1. Solution of Copper Sulphate.—The portion cooled to 20° contained 17.332 per cent. The hot portion at 80° should contain 14.3 per cent.; found, 14.03 per cent.

2. The portion cooled to 20° contained 29.867 per cent. The portion at 80° should contain 24.8 per cent.; found,

23.871 per cent.

It must be stated that previous experiments by Soret gave less favourable results; yet perhaps too much importance

should not be attached to them, owing to the difficulties of experiment.

# IV. Avogadro's Law applied to Dilute Solutions.

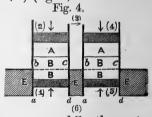
We have considered the changes produced in the osmotic pressure of solutions by alteration of temperature and concentration, and attempted to exhibit the analogy between dilute solutions and gases, in relation to these two quantities. It now remains to compare directly the two analogous quantities, gaseous pressure and osmotic pressure, in one and the same body. It is obvious that this analogy should hold with gases in solution; and in actual fact it will be shown that, if Henry's law be taken into consideration, the osmotic pressure in solution is absolutely equal to the gaseous pressure, under similar conditions of temperature and concentration.

To prove this statement, we shall picture a reversible process by aid of semipermeable diaphragms, temperature being maintained constant; and we shall again make use of the second law of thermodynamics, which in this case leads to the simple result that no work is transformed into heat, nor heat into work; and hence the sum of all work done at different

stages of the process is zero.

This reversible process may be conceived by means of two similar cylinders and pistons, like those already described. One contains a gas (A), say oxygen, and in contact with it a saturated aqueous solution of oxygen (B) (fig. 4). The wall b c

allows only oxygen to pass, but no water; the wall ab, on the other hand, water, but not oxygen; and it is in contact with water, E. A reversible process may be carried out by such an arrangement as follows:—By raising the two pistons (1) and (2), oxygen is



evolved from its aqueous solution as gas, while the water passes through ab; this change can proceed without altering the concentration of the solution. The only difference between the two cylinders is in the state of concentration of the solutions which they contain; we may explain the action thus:— The unit of weight of the substance in question occupies in the left-hand cylinder a volume v and V, and in the right-hand cylinder, v+dv and V+dV; hence, in order that Henry's law may hold,

v: V = (v + dv) : (V + dV); hence v: V = dv : dV. If, now, the pressure, or osmotic pressure, as the case may be (supposing unit volume to contain unit mass), as regards gas and solution be P and p (which will afterwards be shown to be equal), then, from Boyle's law, the pressure in gas and solution will be  $\frac{P}{v}$  and  $\frac{p}{V}$  respectively.

Now let the pistons (1) and (2) be raised so as to liberate unit weight of gas from the solution, and increase the gaseous volume v by dv, in order to equalize its concentration with that of the gas in the left-hand vessel, and by depressing the pistons (4) and (5) let us redissolve the freshly liberated gas, and then reduce the volume of the solution V + dV by the amount dV in the cylinder with semipermeable walls; then

the cycle is complete.

Work has been done in six separate ways; let us number them (1), (2), (3), (4), (5), and (6). Now (2) and (4) are equal in amount, but opposite in sign, since they refer to change of volume v and v+dv in opposite directions under pressures which are inversely proportional to the volumes. In similar manner the sum of (1) and (5) is zero; so that the point requiring proof is that (3)+(6)=0. Here (3) represents work done by the gas in increasing its volume by dv, under a pressure of  $\frac{P}{v}$ , therefore  $(3)=\frac{P}{v}dv$ ; while (6) represents the work done by the solution, while it decreases in volume by dV, under a pressure of  $\frac{P}{V}$ , therefore  $(6)=-\frac{P}{V}dV$ . The statement is therefore

$$\frac{P}{v} dv = \frac{p}{V} dV;$$

and as v: V = dv: dV, P must be equal to p, which was to be proved.

This conclusion, which will receive in the sequel ample confirmation, lends, on the one hand, support to Gay-Lussac's law in its application to liquids:—If gaseous pressure and osmotic pressure are at the same temperature equal to one another, then equal changes of temperature must affect both equally. On the other hand, this relation allows of a considerable extension of Avogadro's law, always provided that we may substitute the conception of osmotic pressure for gaseous pressure:—under equal osmotic pressures and at the same temperature, equal volumes of all solutions contain equal numbers of molecules; and, moreover, the same number of molecules which would be contained in an equal volume of a gas under the same conditions of temperature and pressure.

V. General Expression for Boyle's, Gay-Lussac's, and Avogadro's Laws for Solutions and Gases.

The well-known formula expressing both Boyle's and Gay-Lussac's laws for gases,

PV = RT

are, in so far as these laws are applicable to liquids, also applicable as regards osmotic pressure; with the reservation, also made in the case of gases, that the space occupied by the molecules must be so great that the actual volume of the

molecules becomes negligible.

To include Avogadro's law in the above expression, Horstmann's suggestion (Berl. Ber. xiv. p. 1243) may be adopted, to express the molecular weight of the substance in kilograms; taking 2 kilos. of hydrogen, 44 kilos. of carbon dioxide, and so on. Then R in the above equation has always the same value; for, under equal conditions of temperature and pressure, these weights occupy the same volume. Calculating this value, and expressing the volume in cubic metres, and the pressure in kilograms per square metre, and choosing hydrogen gas at 0° and 760 millim. pressure as starting-point, then

$$P=10333$$
;  $V=\frac{2}{0.08956}$ ;  $T=273$ ;  $R=845.05$ .

Hence the combined expression for Boyle's, Gay-Lussac's, and Avogadro's laws becomes

$$PV = 845 T$$
;

and this expression is applicable to solutions, substituting

osmotic pressure for gaseous pressure.

We may give this equation even a simpler form, inasmuch as the number of calories equivalent to a kilogrammetre of work  $(A = \frac{1}{J} = \frac{1}{423})$  stands in a very simple relation to R, viz. AR = 2 (in reality about one thousandth less). Hence we may choose the form

$$APV = 2T$$
;

and this form has the great practical advantage that work, which will often be discussed in the following pages, receives a very simple expression, if calculated back to heat, measured in calories.

Let us next calculate the work, expressed in calories, when a gas or a solution, under constant pressure and temperature, expands V volumes; V volumes containing a kilogrammolecule. This is evidently 2T. It must be added that this

constant pressure is maintained only when the total volume of gas or solution is very great compared with V, or in cases of evaporation, where the vapour-pressure is at its maximum.

We shall also often have to express in calories the work done during isothermal expansion of the kilogram-molecule of a substance as gas, or in solution. If pressure falls a very small fraction  $\Delta P$ , corresponding to a small increase of volume  $\Delta V$ , the work done will be  $AP\Delta V$ , or  $2\Delta T$ .

# VI. First Confirmation of Avogadro's Law in its Application to Solutions.—Direct determination of Osmotic Pressure.

It is to be expected that Avogadro's law, deduced as a consequence of Henry's law for solutions of gases, will not be restricted to solutions of substances which usually exist in a gaseous condition. This expectation has been realized, not merely from a theoretical, but from an experimental standpoint. Pfeffer's determinations of the osmotic pressure of solutions of sugar furnish a remarkable confirmation of this extension of the law.

Pfeffer's solution consisted of 1 gram of sugar dissolved in 100 grams of water; one gram of the sugar therefore exists in about 100.6 cubic centim. of the solution. Comparing the osmotic pressure of this solution with the pressure of a gas (e. g. hydrogen) containing as many molecules in the volume, there are  $_{342}^{2}$  gram ( $C_{12}H_{22}O_{11}=342$ ) in 100.6 cubic centim. Now one litre of hydrogen gas at  $0^{\circ}$  and 760 millim. pressure weighs 0.08956 gram; and the above concentration is equivalent to 0.0581 gram per litre; the pressure at  $0^{\circ}$  is 0.649 atmosphere, and at t, 0.649(1+0.00367t). Placing these results beside Pfeffer's, we obtain the following agreement:—

Temperature $(t)$ .	Osmotic pressure.	0.649(1+0.00367 t).
6.8	0.664	0.665
13.7	0.691	0.681
14.2	0.671	0.682
15.5	0.684	0.686
22.0	0.721	0.701
32.0	0.716	0.725
36.0	0.746	0.735

The directly determined osmotic pressure of a solution of sugar is thus seen to be equal to the pressure of a gas at the same temperature, containing the same number of molecules in unit volume as the sugar-solution.

Starting from cane-sugar, this relation can be calculated for other dissolved substances, such as invert sugar, malic acid, tartaric acid, citric acid, magnesium malate and citrate, all of which, from de Vries' physiological researches (*Eine Methode zur Messung der Turgorkraft*, p. 512), exhibit equal osmotic pressure when they contain an equal number of molecules in a given volume.

VII. Second Confirmation of Avogadro's Law in its Application to Solutions.—Molecular lowering of Vapour-pressure.

The relation between osmotic pressure and the pressure of a vapour in contact with liquid, which is easily developed on thermodynamical principles, yields, from Raoult's recent observations, a satisfactory proof of the analogy under consideration.

We shall begin with a general law, of which the previous matter of this thesis is quite independent:—Isotonism (i.e. equal osmotic pressure—from "oos and tovos, stretching) in solutions made with the same solvent, implies equality of vapour-pressure. This statement is easily proved by a reversible cycle, keeping temperature constant. Imagine two solutions exhibiting equal vapour-pressure, and introduce a small quantity of one in the state of vapour into the other in a reversible manner, i.e. by means of cylinder and piston. The vapour-pressures are equal, hence this transference takes place without expenditure of work; and also, on restoring the original condition, no work is expended. But if the solvent be transferred back through a semipermeable diaphragm, separating the two solutions, then equal osmotic pressure must exist, else the transference could not take place without expenditure of energy.

If this fundamental conception be applied to dilute solutions, accepting the laws which have been explained in the preceding pages, the simple conclusion follows, that if a solvent contains equal numbers of molecules of dissolved substances, the vapour-pressure is the same. This is merely Raoult's law (Comptes rendus, lxxxvii. p. 167; xliv. p. 1431) of the constancy of molecular diminution of vapour-pressure, obtained by multiplying the relative diminution by the molecular weight of a one-per-cent. solution; i. e. with the difference between the vapour-pressures of the solvent, before and after addition of dissolved substance. The equality of molecular diminution of vapour-pressure depends on the solutions containing equal numbers of molecules, a close proportionality between the lowering of the vapour-pressure and the concentration being assumed. With ether, for example, the value fluctuated between 0.67 and 0.74 (mean 0.71) for thirteen substances

dissolved in it.

But this relation can be further developed. Different solutions may be compared with each other, and a second law may be deduced, which Raoult has also discovered experimentally. The following reversible process, consisting of two operations, is carried out with a very dilute solution of P per cent., at temperature T.

1. Remove, by use of cylinder with semipermeable wall, a portion of the solvent containing a kilogram-molecule (M) of the dissolved substance: here the total quantity of solution is supposed so great that no alteration of concentration occurs,

and the expenditure of work is therefore 2T.

2. This quantity,  $\frac{100\,\mathrm{M}}{\mathrm{P}}$  kilograms, of the solvent is returned as vapour; it may be conceived as produced from the liquid by evaporation at its vapour-pressure; then expanded till its pressure is equal to the vapour-pressure of the solution; and finally liquefied in contact with the solution. The kilogrammolecule of the solvent (M') will thus receive an expenditure of work of  $2\mathrm{T}\Delta$ , where  $\Delta$  represents the relative diminution of pressure; and the  $\frac{100\,\mathrm{M}}{\mathrm{P}}$  kilograms will receive  $2\mathrm{T}\Delta\frac{100\,\mathrm{M}}{\mathrm{P}\mathrm{M'}}$ . Here  $\frac{\Delta}{\mathrm{P}}$  M is Raoult's molecular diminution of pressure, which we shall term K; employing this abbreviation, the expression becomes  $\frac{200\,\mathrm{T}\mathrm{K}}{\mathrm{M'}}$ .

From the second law of thermodynamics, again, the algebraic sum of the work expended during this cycle at constant pressure must equal zero; hence the work done by the solution during the first stage must equal the work done on it during the second; and thus

$$2T = \frac{200 \, TK}{M'}$$
; or  $100 \, K = M'$ .

This expression includes all Raoult's results. It expresses the fact, as stated above, that the molecular diminution of vapour-pressure is independent of the nature of the dissolved body; and it also expresses, what Raoult found experimentally, that this diminution is independent of temperature. It also contains Raoult's second conclusion, that the molecular diminution is proportional to the molecular weight of the solvent, amounting to about one hundredth of the latter. This is seen from the following table:—

Solvent.	Molecular weight. (M').	Molecular diminution of vapour- pressure. (K).
Water	. 18	0.185
Phosphorous chloride.	. 137.5	1.49
Carbon disulphide	. 76	0.80
Carbon tetrachloride.	. 154	1.62
Chloroform	. 119.5	1.30
Amylene	. 70	0.74
Benzene	. 78	0.83
Methyl iodide	. 142	1.49
Methyl bromide	. 109	1.18
Ether	. 74	0.71
Acetone	. 58	0.59
Methyl alcohol	. 32	0.33

VIII. Third Confirmation of Avogadro's Law in its Application to Solutions.—Molecular Depression of Freezing-point of Solvent.

Here, again, a general law may be stated, connecting osmotic pressure with the freezing-point of a solution:—Solutions in the same solvent, and of the same freezing-point, are isotonic at that temperature. This statement admits, like the former, of proof by means of a reversible cycle; but the solvent when returned is here in the condition of ice, not of vapour; the inverse change is also brought about by means of a semipermeable diaphragm, and, as it cannot be accompanied by gain or loss of energy, isotonism must exist.

We shall apply the above statement to dilute solutions: and applying the relations previously described, the simple conclusion follows that solutions containing an equal number of molecules in equal volume, and which therefore, from Avogadro's law, are isotonic, also have the same freezing-point. This law has been actually discovered by Raoult, and is expressed by him as "normal molecular depression of freezingpoint." It holds for the great majority of dissolved substances examined, and consists in the statement that the depression of freezing-point of a one-per-cent. solution, multiplied by the molecular weight of the dissolved substance, gives a constant product; it is stated of solutions containing equal numbers of molecules in unit volume, assuming a close proportionality between concentration and lowering of the freezing-point. For an aqueous solution of nearly all organic bodies the constant product is about 18.5.

We can follow this relation still further, and, assuming Avogadro's law for solutions, deduce the above normal molecular depression of the freezing-point from other data. It bears a close relation to the heat of fusion of the solvent, as is shown by applying the second law of thermodynamics to a reversible cycle. Imagine a very dilute solution containing P per cent. of a dissolved substance, which has produced a depression of freezing-point,  $\Delta$ ; the solution itself freezes at T, and its heat of fusion is W per kilogram.

1. By use of piston and cylinder with semipermeable walls, the solution is deprived at temperature T of that amount of the solvent in which a kilogram-molecule of the dissolved substance existed; the amount of the solution is moreover so great that no appreciable change of concentration occurs,

hence the work expended on it is 2T.

2. This quantity of solvent,  $\frac{100 \text{ M}}{P}$ , is then allowed to freeze at T by withdrawing  $\frac{100 \,\mathrm{MW}}{\mathrm{P}}$  calories; the solution and the solvent, now solid, are cooled through  $\Delta$  degrees, and the

solvent is now allowed to melt in contact with the solution, thereby absorbing the above quantity of heat. Finally, the

temperature is raised  $\Delta$  degrees.

During this reversible process  $\frac{100 \,\mathrm{MW}}{\mathrm{P}}$  calories rise from  $\Delta$  to T, corresponding to an expenditure of energy equal to  $\frac{100\,\mathrm{MW\Delta}}{\mathrm{PT}}$ . In this expression, however,  $\frac{\mathrm{M\Delta}}{\mathrm{P}}$  is the molecular depression of the freezing-point, which we may represent by the letter t; the work done is therefore  $\frac{100 \,\mathrm{W} t}{\mathrm{T}}$ , and it was shown above to be equal to 2T. Hence the equation

$$\frac{100 \,\mathrm{W}t}{\mathrm{T}} = 2\mathrm{T} \; ; \text{ whence } t = 0.02 \; \frac{\mathrm{T}^2}{\mathrm{W}}.$$

This theoretical deduction receives ample confirmation from experimental data. The following table exhibits the molecular depression of freezing-point experimentally determined by Raoult (Annales de Chimie et de Physique, [5] xxviii.; [6] xi.), along with the values calculated by means of the above formula:-

Solvent.	Freezing- point	Heat of fusion	$t = \frac{0.02 \mathrm{T}^2}{\mathrm{W}}.$	Raoult's molecular
Water	T).	(W). 79	18.9	depression.
.,	273 + 16.7	43.2*†	38.8	18·5 38·6
Formic acid		55.6*†	28.4	27.7
Benzene .		29.1	53	50
Nitrobenzene	273 + 5.3	22.3†	69.5	70.7

It may be added that, from the molecular depression of ethylene bromide (117.9), the hitherto unknown heat of fusion is found equal to 13; and Mr. Pettersson, at my request, having experimentally determined this constant, obtained the number 12.94.

# IX. Application of Avogadro's Law to Solutions.—The Law of Guldberg and Waage.

Having discussed the physical aspect of this problem in order to furnish as many proofs as possible of the correctness of its treatment, it now remains to apply it to chemical facts.

The most evident application of Avogadro's law in reference to solutions is to the determination of the molecular weights of dissolved substances. This has already been attempted; but here it is not the pressure which requires measurement, as with gases, when the molecular weight is deducible from volume, pressure, and temperature; with solutions the osmotic pressure must be measured, and as yet the practical method is wanting. Yet this difficulty may be avoided by substituting for a determination of pressure that of the related values; as, for example, the diminution of vapour-pressure, or the depression of the freezing-point. This proposal is Raoult's. He divides the reduction of vapour-pressure of water containing one per cent. of dissolved substance into 0.185 parts, or the observed depression of freezing-point into 18.5 parts; and this method is comparable in respect of accuracy with determinations of the density of gases, and is in itself a strong presumption of the accuracy of Avogadro's law in its application to gases.

It is still more remarkable that the law of Guldberg and Waage, so generally accepted for solutions, can be evolved from the above laws regulating the behaviour of dilute solutions. Again, a reversible cycle at constant temperature must be imagined, which can be conceived for solutions equally well with gases, by means of semipermeable

diaphragms.

<sup>\*</sup> Berthelot, Essai de Mécanique Chimique. † Pettersson, Journ. f. prakt. Chem. [2] xxvi. p. 129.

Let there be two systems of gaseous or dissolved substances in equilibrium, which may be expressed by the following symbols:—

$$a_i' M_i' + a_i'' M_i'' + &c. a_{ii}' M_{ii}' + a_{ii}'' M_{ii}'' + &c.,$$

where a denotes the number of molecules, and M the formula. This equilibrium exists in two different vessels, A and B, at the same temperature but at different concentrations, shown by the partial pressure, or by the osmotic pressure which each of the bodies exerts. Let these pressures be in vessel A,  $P'P'' \dots P'_{n}P''_{n}$  &c.; and in B greater than these by  $dP'_{n}D''_{n}$  decreases.

The reversible cycle consists in introducing into A that amount in kilograms expressed by the first symbol of the first system, while the second is removed in equivalent amount: both systems have here the concentrations which exist in A

(fig. 5). This change is accomplished by causing the entry or exit of each of the substances in question by means of its own cylinder and piston, which is separated from A by a diaphragm permeable to that body alone. If they are in solution, then the cylinders possess a semipermeable wall, and are surrounded by the solvent.

When this has been done, each constituent of the two systems has

undergone such a change of concentration that it is now equal to that in B; and, as before, the work done per kilogrammolecule equals  $2\Delta T$ , where  $\Delta$  represents a minute fraction of the pressure, and is here  $\frac{dP}{P}$ ; for the amounts here in question it is  $2aT\frac{dP}{P}$ .

By making use of the vessel B, the second system, which has just been evolved, is now converted into the first, but of concentration as in B, proceeding as just described; and by suitable alteration of volume it is finally changed into its original state, as it at first existed in A.

As no change of temperature has occurred, the algebraic sum of all these operations is zero, as is seen from the numbers; it is thought unnecessary to interpret them, as they refer to the operations in the order in which they were carried out:— (1)+(2)+(3)+(4)+(5)+(6)=0.

Now (1) and (5) refer to operations opposite in sign on the same substances, with the same mass, at the same temperature; hence (1)+(5)=0. And for similar reasons, (2)+(4)=0; whence (3) + (6) = 0.

This conclusion leads directly to Guldberg's and Waage's

law.

The work expressed by (3) is from that law  $\Sigma 2a_{\mu}T\frac{dP_{\mu}}{P_{\mu}}$ , and (6) is  $\Sigma 2a_{\nu}T\frac{dP_{\mu}}{P_{\mu}}$ ; hence it follows that

$$\Sigma \left(2a_{ii}T\frac{dP_{ii}}{P_{ii}}-2a_{ii}T\frac{dP_{i}}{P_{i}}\right)=0$$
, or  $\Sigma \left(a_{ii}\frac{dP_{ii}}{P_{ii}}-a_{i}\frac{dP_{i}}{P_{i}}\right)=0$ .

By integrating,

$$\Sigma(a_{ii} \log P_{ii} - a_{ii} \log P_{ii}) = \text{constant};$$

and here P is proportional to the concentration, or to the active mass C; so that C may be substituted without altering the equation:—

$$\Sigma(a_{ii} \log C_{ii} - a_{i} \log C_{i}) = \text{constant.}$$

This is the logarithmic form of Guldberg's and Waage's formula.

## X. Deviation from Avogadro's Law in Solutions.—Variations in Guldberg and Waage's Law.

We have attempted to show the connexion between Guldberg and Waage's law and the laws of Boyle, Henry, Gay-Lussac, and Avogadro, as applied to liquids; as applied to gases, the truth of Guldberg and Waage's law has been long proved from thermodynamical considerations.

It remains to develop further the laws of chemical equilibrium, and, first, to investigate more closely the limits of applicability of the three fundamental principles from which

Guldberg and Waage's law has been deduced. So long as "ideal solutions" are under consideration, there exists strict analogy between gases and solutions; and just as there are deviations from Avogadro's law in the case of gases, so we may expect to find them with solutions. for example, the pressure of the vapour of ammonium chloride was found to be too great to be accounted for by Avogadro's law, so the osmotic pressure is in many cases abnormal; and as the high pressure in the first case is due to dissociation into ammonia and hydrogen chloride, it may be conceived that similar dissociation occurs in solutions. It must, indeed, be acknowledged that deviations are much more frequent with solutions than with gases, and occur often with bodies the

dissociation of which, under ordinary circumstances, does not appear probable; in aqueous solution, for example, the majority of salts as well as the stronger acids and bases undergo dissociation; and hence Raoult did not discover the existence of so-called normal molecular depression of freezing-point and lowering of vapour-pressure until he investigated organic compounds; their behaviour is almost without exception regular. For these reasons it may have appeared daring to begin by giving prominence to Avogadro's law in its application to solutions; and I should have shrunk from this course had not Arrhenius pointed out to me the probability that salts, and analogous bodies, decompose on solution into their ions; in fact, substances which obey Avogadro's law are, as a rule, non-conductors, suggesting that in such cases no dissociation into ions occurs; and further experimental proof exists for other liquids, since by Arrhenius's assumption the deviations from Avogadro's law are calculable from the conductivity.

However this may stand, an attempt is made in the following pages to take account of such deviations from Avogadro's law, and, by help of the application of Boyle's and Gay-Lussac's laws to solutions, to develop Guldberg's and Waage's

formula so far as is possible.

The change in the expressions given above caused by these

deviations is easily sketched.

The general expression for Boyle's, Gay-Lussac's, and Avogadro's laws, shown on p. 90, is

$$APV = 2T$$
;

and this changes, if pressure is i-times that of this equation, into

$$APV = 2 i T$$
.

Hence, in a reversible cycle, the work will be *i*-times that previously done; this alteration is easily applied to the former statement of Guldberg's and Waage's formula. Recurring to the final stage of the cycle described on p. 97,

$$(3) + (6) = 0,$$

the work corresponding to (3) and (6), which were formerly  $\Sigma 2a_{i}T\frac{dP_{i}}{P_{i}}$ , and  $-\Sigma 2a_{i}T\frac{dP_{i}}{P_{i}}$ , is now increased *i*-times; hence the equations become

$$\Sigma \left( a_{i}i_{i}\frac{dP_{i}}{P_{ii}} - a_{i}i_{i}\frac{dP_{i}}{P_{i}} \right) = 0;$$

and on integration,

$$\Sigma(a_{i}, i_{i}, \log P_{i}, -a_{i}, \log P_{i}) = \text{constant.}$$

And introducing the concentration, or the active mass C, instead of the pressure proportional to it,

 $\Sigma(a_{\mu}i_{\mu}\log C_{\mu}-a_{\mu}i_{\mu}\log C_{\mu}) = \text{constant.}$ 

This is Guldberg's and Waage's law in a logarithmic form, differing from the former statement only by the introduction of the value i.

It remains to be shown that in this new form it agrees better with experimental results; and as a knowledge of the correct value of *i* is necessary, we must deal with aqueous solutions, for sufficient experimental data are to be had only with such.

# XI. Determination of i for Aqueous Solutions.

As Avogadro's law has been proved for solutions by four separate lines of argument, there are four ways in which the deviations, i. e. the values of i, may be determined. But that one which depends on the lowering of the melting-point has been so thoroughly proved experimentally that we shall confine ourselves to its use.

Reverting to the cycle which, on p. 95, was employed to prove the applicability of Avogadro's law to solutions, the relation was found:—

$$\frac{100 \text{ W}t}{\text{T}} = 2\text{T},$$

where the second term refers to the work done in removing or adding that amount of the solvent in which a kilogram-molecule of the substance was dissolved; that term must therefore be multiplied by i:—

$$\frac{100 \text{ W}t}{\text{T}} = 2i\text{T}.$$

In this manner a simple means of determining the value of i is apparent. The value of i is from the above equation proportional to t, i. e. to the molecular depression of temperature, for the other data (T=absolute melting-point, W=heat of fusion of solvent) are constant. Now 18.5 is the molecular depression for cane-sugar, which from p. 91 is seen to follow Avogadro's law accurately; hence i=1; and for other bodies i is their respective depressions divided by 18.5. Almost identical results are arrived at by using in the above equation, instead of T and W, the values for ice, viz. 273 and 79; they will therefore be employed in the following calculations.

# XII. Proof of the Modified Law of Guldberg and Waage.

In employing the relation proposed for the purpose of comparison with the results of Guldberg and Waage's formula,

it is necessary to mention the different forms which it has assumed during the years since its discovery. We shall first give this relation a simple expression in which Guldberg and Waage's conceptions may be included, viz.:—

$$\sum ai \log C = K.$$
 . . . . (1)

This differs from the one given on p. 100 merely in that the terms representing the components of both systems have had their signs changed. The original expression of the Norwegian investigators is closely analogous (*Christiania Videnskabs Selskabs Forhandlingar*, 1864):—

$$\sum k \log C = K \dots \dots (2)$$

except that k has to be determined for each constituent in question by observation of the equilibrium of the system.

As Guldberg and Waage (Études sur les affinités chimiques, 1867) repeatedly found the coefficient k equal to 1, they simplified their equation thus:—

$$\Sigma \log C = K.$$
 . . . . . (3)

In their last treatise, however (Jour. für prakt. Chem. xix. p. 69), they introduce the change that the number of molecules a must also be taken account of, and consequently they approximate their formula to that deduced for gases on thermodynamical grounds, thus:—

$$\Sigma a \log C = K$$
; . . . . . (4)

We have taken this last expression as their final formula.

The Norwegian investigators maintained this simple formula, with whole numbers as coefficients, even for solutions; but Lemoine has lately revived the original formula (2) in order to represent the results of Schlösing's investigations on the solubility of calcium carbonate in water containing carbon dioxide, with constants hereafter to be determined, which are, however, not whole numbers; for if whole numbers be employed, it is impossible to reconcile fact with theory.

In view of this uncertainty, the formula which we have suggested has this advantage, that the coefficients which occur in it are à priori determined, and its truth can at once be decided by experiment. It will in fact appear that in the instances studied by Guldberg and Waage the simple form which they recommend is completely confirmed; and that such simplification is in most cases admissible confirms, moreover, the validity of Avogadro's law in its application to solutions. On the other hand, the results of Schlösing's investigation, prominently alluded to by Lemoine, cannot be

simply expressed, and require the same fractional coefficients

which Schlösing himself arrived at.

Before proceeding to this investigation, it is necessary to include cases where partially insoluble bodies are present: this is easily done; they may be included in the formulæ given above, remembering that such bodies exist in solution up to its saturation-point, and are therefore present with constant concentration. All concentrations depending on this may, therefore, be removed from the first term of the above equation to the second, without affecting the constancy of the latter. Everything remains the same, except that in the first term only the dissolved bodies need be considered.

1. We shall first examine Guldberg and Waage's observations. The first case they studied was that expressed by the

equation

$$BaCO_3 + K_2SO_4 \Rightarrow BaSO_4 + K_2CO_3$$
;

and they found, according to their simplified formula, that

$$\log C_{K_2SO_4} - \log C_{K_2CO_3} = K.$$

The relation given by our equation is almost identical, for, for  $K_2SO_4$ , a=1 and  $i=2\cdot11$ , and for  $K_2CO_3$ , a=1 and  $i=2\cdot26$ ; hence

$$\log\,\mathrm{C}_{K_2^*O_4} {-}\, 1.07\,\log\,\mathrm{C}_{K_2CO_3} {=}\, \mathrm{K}.$$

A similar agreement exists with sodium carbonate, for then the values of i for  $Na_2SO_4$  and  $Na_2CO_3$  are 1.91 and 2.18 respectively; hence

2. This result, expressed in what is almost a whole number, cannot be expected in the above-mentioned experiment of Schlösing (Comptes rendus, lxxiv. 1552; lxxv. 70). There the subject of experiment was the solubility of calcium carbonate in water containing carbonic acid, and the state of equilibrium is expressible by the following statement:—

$$CaCO_3 + H_2CO_3 \stackrel{\sim}{\sim} Ca(HCO_3)_2$$
.

We should expect that, as i=1 for carbon dioxide, that i should =2 56 for calcium hydrogen carbonate:—

and Schlösing found:-

$$0.37866 \log C_{H_2CO_3} - \log C_{Ca(HCO_3)_2} = K.$$

Similar experiments with barium are equally satisfactory; the value of *i* for barium hydrogen carbonate is 2.66, and the following results are calculated:—

The experimental result is

3. Turning to Thomsen's investigation on the action of sulphuric acid on sodium nitrate in solution (Thomsen's Thermochemische Untersuchungen, i.), we find a similar agreement.

The reaction may be formulated thus:-

$$Na_2SO_4 + HNO_3 \sim NaHSO_4 + NaNO_3$$
;

and Guldberg and Waage's relation requires

$$\begin{array}{c} \log \, C_{Na_2SO_4} \! + \! \log \, C_{HNO_3} \! - \! \log \, C_{NaHSO_4} \! - \! \log \, C_{NaNO_3} \! = \! K. \\ Now \end{array}$$

 $i_{\text{Na}_2\text{SO}_4}$ =1·91;  $i_{\text{HNO}_3}$ =1·94;  $i_{\text{NaHSO}_4}$ =1·88; and  $i_{\text{NaNO}_3}$ =1·82; and the equation becomes

$$\begin{array}{c} 1.05 \, \log \, \mathrm{C_{Na_2SO_4}} \! + 1.06 \, \log \, \mathrm{C_{HNO_3}} \! - 1.03 \, \log \, \mathrm{C_{NaHSO_4}} \\ - \log \, \mathrm{C_{NaNO_3}} \! = \! \mathrm{K_{2}}. \end{array}$$

which is almost identical.

If we express the relation thus:-

$$Na_2SO_4 + 2HNO_3 \rightleftharpoons H_2SO_4 + 2NaNO_3$$

Guldberg and Waage's formula becomes

 $\log C_{Na_2SO_4} + 2 \log C_{HNO_3} - \log C_{H_2SO_4} - 2 \log C_{NaNO_3} = K$ ; and we obtain :

$$\begin{array}{c} \log \, \mathrm{C_{Na_{3}SO_{4}}} \! + \! 2 \! \cdot \! 03 \, \log \, \mathrm{C_{HNO_{3}}} \! - \! 1 \! \cdot \! 07 \, \log \, \mathrm{C_{H_{2}SO_{4}}} \\ -1 \! \cdot \! 91 \, \log \, \mathrm{C_{NaNO_{3}}} \! = \! K \ ; \end{array}$$

Again an almost absolute agreement.

4. Ostwald's investigation (J. prakt. Chem. [2] xix. p. 480) on the action of hydrochloric acid on zinc sulphide, according to the formula

$$ZnS + 2HCl \stackrel{\rightarrow}{=} H_2S + ZnCl_2$$
,

leads, when the following values are ascribed:

$$i_{\text{HCl}} = 1.98$$
;  $i_{\text{H}_2\text{S}} = 1.04$ ;  $i_{\text{ZnCl}_2} = 2.53$ 

to the equation :-

It is evident that the concentrations of the sulphuretted hydrogen and the zinc chloride are equal, for only hydrochloric acid and zinc sulphide are initially present. The result is expressible by taking the volume V, in which a known amount of hydrochloric acid was dissolved, as the

initial concentration; and the fraction x to denote that portion which after contact with zinc sulphide has finally reacted, forming zinc chloride. Hence we have

$$3.96 \log \frac{1-x}{V} - 3.57 \log \frac{x}{V} = \text{const.};$$

and also

$$\frac{x}{(1-x)^{1\cdot 1}}V^{0\cdot 1} = \text{const.}$$

This function is really nearly constant:

Volume (V).	Portion reacted $(x)$ .	$\frac{x}{(1-x)^{1\cdot 11}} \nabla_{0\cdot 11}$
1	0.0411	0.043
2	0.038	0.0428
4	0.0345	0.0418
8	0.0317	0.0413

Similar experiments with sulphuric acid, where *i* for H<sub>2</sub>SO<sub>4</sub> and ZnSO<sub>4</sub> is respectively 2.06 and 0.98, gave

$$\frac{x}{(1-x)^{1.02}}$$
  $V^{0.02} = \text{const.};$ 

and here also x is nearly a constant, as is seen from the following experimental numbers:—

Volume V.	Portion reacted (x).
2	0.0238
4	0.0237
8	0.024
16	0.0241

5. The experiments of Engel on the solubility of magnesium carbonate in water containing carbonic acid (*Comptes rendus*, c. pp. 352, 444) also deserve notice. The state of equilibrium is

$$MgCO_3 + H_2CO_3 \stackrel{>}{\sim} Mg (HCO_3)_2$$
;

and our formula leads to the following relation, where i=2.64 for acid magnesium carbonate:—

$$0.379 \log C_{H_2CO_3} - \log C_{Mg(HCO_3)_2} = K.$$

The number found was

$$0.370 \log C_{H_2CO_3} - \log C_{Mg(HCO_3)_2} = K.$$

6. Other experiments by the same author on the simultaneous solubility of copper and ammonium sulphates (Comptes rendus, cii. p. 113), are shown by the reversible equation

$$CuSO_4 + (NH_4)_2SO_4 = Cu(NH_4)_2(SO_4)_2$$
.

As the double salt was always partly undissolved, and as the values of i for  $CuSO_4$  and for  $(NH_4)_2SO_4$  are 0.98 and 2.0, we have the relation

$$0.49 \log C_{\text{CuSO}_4} - \log C_{(NH_4)_2SO_4} = K.$$

The number found is 0.438 log C<sub>cuso4</sub>.

7. In conclusion, we may notice Le Chatelier's experiments on the equilibrium between basic mercuric sulphate and sulphuric acid (*Comptes rendus*, xevii. p. 1565);

In this case the values of i for  $\rm H_2SO_4$  and  $\rm HgSO_4$  are 2.06 and 0.98, and we have

1.4 log 
$$C_{H_2SO_4}$$
 – log  $C_{HgSO_4}$  = K.

The found value is  $1.58 \log C_{H_2SO_4}$ .

Generally speaking, therefore, such results show a very satisfactory agreement.

XIII. On an Explanation of the Action of a Magnet on Chemical Action. By Henry A. Rowland and Louis Bell\*.

IN the year 1881 Prof. Remsen discovered that magnetism had a very remarkable action on the deposition of copper from one of its solutions on an iron plate, and he published an account in the American Chemical Journal for the year 1881. There were two distinct phenomena then described—the deposit of the copper in lines approximating to the equipotential lines of the magnet, and the protection of the iron from chemical action in lines around the edge of the poles. It seemed probable that the first effect was due to currents in the liquid produced by the action of the magnet on the electric currents set up in the liquid by the deposited copper in contact with the iron plate. The theory of the second kind of action was given by one of us, the action being ascribed to the actual attraction of the magnet for the iron, and not to the magnetic state of the latter. It is well-known since the time of Faraday that a particle of magnetic material in a magnetic field tends to pass from the weaker to the stronger portions of the field; and this is expressed mathematically by stating that the force acting on the particle in any direction is proportional to the

<sup>\*</sup> Communicated by the Authors, having been read at the Manchester Meeting of the British Association, September, 1887.

rate of variation of the square of the magnetic force in that direction. This rate of variation is greatest near the edges and points of a magnetic pole, and more work will be required to tear away a particle of iron or steel from such an edge or point than from a hollow. This follows whether the tearing away is done mechanically or chemically. Hence the points and edges of a magnetic pole, either of a permanent or induced

magnet, are protected from chemical action.

One of Prof. Remsen's experiments illustrates this most beautifully. He places pieces of iron wire in a strong magnetic field, with their axes along the lines of force. On attacking them with dilute nitric acid they are eaten away until they assume an hourglass form, and are furthermore pitted on the ends in a remarkable manner. On Prof. Remsen's signifying that he had abandoned the field for the present, we set to work to illustrate the matter in another manner, by means of the electric currents produced from the change in the electrochemical nature of the points and hollows of the iron.

The first experiments were conducted as follows:—Two bits of iron or steel wire about 1 millim. in diameter and 10 millim. long were imbedded side by side in insulating material, and each was attached to an insulated wire. One of them was filed to a sharp point, which was exposed by cutting away a little of the insulation, while the other was laid bare on a portion of the side. The connecting wires were laid to a reflecting-galvanometer, and the whole arrangement was placed in a small beaker held closely between the poles of a large electromagnet, the iron wires being in the direction of the lines of force. When there was acid or any other substance acting upon iron in the beaker, there was always a deflection of the galvanometer due to the slightly different action on the two poles. When the magnet was excited the phenomena were various. When dilute nitric acid was placed in the beaker and the magnet excited, there was always a strong throw of the needle at the moment of making circuit, in the same direction as if the sharp-pointed pole had been replaced by copper and the other by zinc. This throw did not usually result in a permanent deflection, but the needle slowly returned towards its starting point, and nearly always passed it and produced a reversed deflection. This latter effect was disregarded for the time being, and attention was directed to the laws that governed the apparent "protective throw," since the reversal was so long delayed as to be quite evidently due to after effects and not to the immediate action of the magnet.

With nitric acid this throw was always present in greater or less degree, and sometimes remained for some minutes as a temporary deflection, the time varying from this down to a few seconds. The throw was independent of direction of current through the magnet, and apparently varied in amount with the strength of acid and with the amount of deflection due to the original difference between the poles. This latter fact simply means that the effect produced by the magnet is more noticeable as the action on the iron becomes freer.

When a pair of little plates exposed in the middle were substituted for the wires, or when the exposed point of the latter was filed to a flat surface, the protective throw disappeared, though it is to be noted that the deflection often gradually reversed in direction when the current was sent through the magnet; i.e. only the latter part of the previous phenomenon appeared under these circumstances.

When the poles, instead of being placed in the field along the lines of force, were held firmly perpendicular to them, the protective throw disappeared completely, though as before

there was a slight reverse after-effect.

Some of Prof. Remsen's experiments on the corrosion of a wire in strong nitric acid were repeated with the same results as he obtained, viz. the wire was eaten away to the general dumbbell form, though the protected ends instead of being club-shaped had the ends perceptibly hollowed. When the wire thus exposed was filed to a sharp point the extreme point was very perfectly protected, while there was a slight tendency to hollow the sides of the cone, and the remainder of the wire was as in the previous experiments. In both cases the bars were steel and showed near the ends curious corrugations, the metal being left here and there in sharp ridges and points. In one case the cylinder was eaten away on sides and ends, so that a ridge of almost knife-like sharpness was left projecting from the periphery of the ends.

These were the principal phenomena observed with nitric acid. Since this acid is the only one which attacks iron freely in the cold, in Prof. Remsen's investigations this was the one to which experiments were in the main confined. With the present method, however, it was possible to trace the effect of the magnet whenever there was the slightest action on the iron, and consequently a large number of substances, some of which hardly produce any action, could be used with not a little

facility.

In thus extending the experiments some difficulties had to be encountered. In many cases the action on the iron was so irregular that it was only after numerous experiments under widely varying conditions that the effect of the magnet could be definitely determined. Frequently the direction of the original action would be reversed in the course of a series of experiments without any apparent cause, but in such case the direction of the effect due to the magnet always remained unchanged, uniformly showing protection of the point so long as the wires remained parallel to the lines of force. When, however, the original action and the magnetic effect coincided in direction, the repetition of the latter showed a decided ten-

dency to increase the former.

When using solutions of various salts more or less freely precipitated by the iron, it frequently happened that the normal protective throw was nearly or quite absent, but showed itself when the magnetic circuit was broken as a violent throw in the reverse direction, showing that the combination had been acting like a miniature storage battery which promptly discharged itself when the charging was discontinued by breaking the current through the magnet. The gradual reversal of the current some little time after exciting the magnet was noted frequently in these cases, as before. Owing to this peculiarity and their generally very irregular action, the various salts were disagreeable substances to experiment with, though as a rule they gave positive results.

Unless the poles were kept clean experimenting became difficult from the accumulation of decomposition products about them and oxidation of their surfaces. A few experiments showed how easily the original deflection could be modified, nearly annulled, or even reversed in direction by slight differences in the condition of the poles. These difficulties of the method are, however, more than counterbalanced by its rapidity and delicacy when proper precautions are

taken.

Nearly thirty substances were tested in the manner previously described, but comparatively few of them gave very decided effects with the magnet, though, as later experiments have shown, the protective action is a general one. The substances first tried were as follows. The table shows the various acids and salts tried, and their effects as shown by the

original apparatus.

Several things are worthy of note in this list. In the first place those solutions of metallic salts which are precipitated by iron all show distinct signs of protective action when the current is passed through the magnet. Of the various acids this is not generally true, only those showing the magnetic effect which act on iron without the evolution of hydrogen, and are powerful oxidizing agents. In general substances which acted without the evolution of hydrogen gave an effect with the magnet.

Substances.	Effect due to magnet.	Notes.		
Nitric acid	Strong. Little or none.	Always powerful protective throw. Does not act very readily on the iron.		
Hydrochloric acid	None."			
Formic ,,	,,			
Oxalic ,,	19			
Chromic ,,	Some effect.	Sometimes quite distinct throw, irregular.		
Perchloric ,,	None.	Much less marked than with chromic.		
Bromic ,,	27	Hardly any effect on iron.		
Permanganic ,,		More than with perchloric.		
Bromine ,	,,			
Copper sulphate	99	Mainly showing as throw, on breaking.		
" nitrate	Some.	22 22 22		
,, acetate	**	17 19 29		
,, chloride	Slight.	27 27 23		
Mercuric bromide	Some.	Throw, on breaking.		
,, chloride	,,	Very slight solution, weak.		
Mercurous nitrate Ferric chloride	Decided.	Mainly as throw on breaking.  Both protective throw, and sometimes on breaking.		
Silver nitrate	Some.	Action very irregular.		
Platinum tetrachloride .	29	,, ,,		

From these experiments it was quite evident that the protective action, whatever its cause, was more general than at first appeared, and steps were next taken to extend it to the other magnetic metals. Small bars were made of nickel and cobalt, and tried in the same manner as before. These metals are acted on but very slightly by most acids, and the range of substances which could be used was therefore very small, but all the substances which gave the magnetic effect with iron poles gave a precisely similar, though much smaller effect, whenever they were capable of acting at all on the This was notably the case with nitric acid. nickel and cobalt. bromine water, chlorine water, and platinum tetrachloride, which were the substances acting most readily on the metals in question. Even with these powerful agents, however, the magnetic action was very much less than with iron, and experimentation on metals even more weakly magnetic was evidently hopeless.

As a preliminary step towards ascertaining the cause of the magnetic action, and its nonappearance where the active substance evolved hydrogen, it now became necessary to discover and if possible eliminate the cause of the reversal of the current which regularly followed the protective throw. Experiments soon showed that it could not be ascribed to accumulation of decomposition products around the electrodes, and polarization, while it could readily neutralize the original deflection, could not reverse its direction. Whatever the cause, it was one which did not act with any great regularity, and it was soon found that stirring the liquid while the magnet was on uniformly produced the effect observed. Since one pole was simply exposed over a small portion of its side while the other had a sharp projecting point, it was the latter which was most freely attacked when there were currents in the liquid, whether these were stirred up artificially, or were produced by the change in galvanic action due to the presence of the magnet. When the poles were placed in fine sand saturated with acid this reversing action was much diminished, and in fact anything which tended to hinder free circulation of the liquid produced the same effect. Several materials were tried and of these the most successful was an acidulated gelatine, which was allowed to harden around the poles. this case the protective throw was not nearly as large as in the free acid, since the electrodes tended to become polarized while the gelatine was hardening, and only weakly acid gelatine would harden at all; but the reversing action completely disappeared, so that when the magnet was put on, a permanent deflection was produced instead of a transitory

This point being cleared up, attention was next turned to the negative results obtained with acids which attack iron with evolution of hydrogen. The galvanometer was made much more sensitive and removed from any possible disturbing action due to the magnet, and with these precautions the original experiments were repeated, it seeming probable that even if the magnetic effect were virtually annulled by the hydrogen evolved, some residual effect might be observed.

This residual effect was soon detected, first with hydrobromic acid, and then with hydrochloric, hydriodic, sulphuric, and others. The strongest observed effect was with hydriodic acid, but as this may possibly have contained traces of free iodine, it may be regarded as somewhat doubtful. The effect in all these cases was very small, and though now and then suspected in the previous work, could not have been definitely determined, much less measured.

Some rough measurements were made on the electromotive forces involved in this class of phenomena by getting the

throw of the galvanometer for various small known values of the E.M.F. The values found varied greatly, ranging from less than 0.001 volt in case of the acids evolving hydrogen, up to 0.02 or 0.03 volt with nitric acid and certain salts. These were the changes produced by the magnet, while the initial electromotive forces normally existing between the poles would be, roughly speaking, from 0.001 to nearly 0.005 volts, never disappearing and rarely reaching the latter figure.

From these experiments it therefore appears that the protective action of the magnetic field is general, extending to all substances which act chemically on the magnetic metals. While this is so, the strongest effect is obtained with those substances which act without the evolution of hydrogen. But the series is really quite continuous, perchloric acid for instance producing but little more effect than hydrobromic, while this in turn differs less from perchloric than from an It seems probable that the action of the acid like acetic. hydrogen evolved is partially to shield the pole at which it is evolved, and lessen the difference between the poles produced by the magnet. It probably acts merely mechanically, for it is to be noted that those acids which evolve a gas other than hydrogen (perchloric acid for instance), which is not absorbed by the water, tend to produce little magnetic effect compared with those which act without the evolution of any gas.

As to the actual cause of the protective action exercised by the magnetic field, all these experiments go to show that it is quite independent of the substance acting, with the exception above noted, and is probably due to the attractive action of the magnet on the magnetic metals forming the poles subjected

to chemical action, as we have before explained.

In the first place, whenever iron is acted upon chemically in a magnetic field, those portions of it about which the magnetic force varies most rapidly are very noticeably protected. and this protection, as nearly as can be judged, varies very nearly with the above quantity. Wherever there is a point there is almost complete protection, and wherever there is a flat surface, no matter in how strong a field, it is attacked freely. Whenever in the course of the action there is a point formed, the above condition is satisfied and protection at once appears. Thus, in the steel bars experimented on, whenever the acid reached a spot slightly harder than the surrounding portions, it produced a little elevation from which the lines of force diverged, and still further shielding it produced a ridge or point, sharp as if cut with a minute chisel. Nickel and cobalt tend to act like iron, though they are attacked with such difficulty that the phenomena are much less strongly marked. With the non-magnetic metals they are completely absent. Now, turning to the experiments with the wires connected with a galvanometer, the same facts appear in a

slightly different form.

When the poles were placed perpendicular to the lines of force instead of parallel to them, the magnet produced no effect whatever; showing, firstly, that the effect previously observed depended not merely on the existence of magnetic force, but on its relation to the poles, and, secondly, that when the poles were so placed as to produce little deflection of the lines of

force, the protective effect disappeared.

When the pointed pole was blunted the effect practically disappeared, the poles remaining parallel to the lines of force, and when plates were substituted for the wires no effect was produced in any position, showing that the phenomena were not due to the directions of magnetization, but to the nature of the field at the exposed points. In short, whatever the shape or arrangement of the exposed surfaces, if at any point or points the rate of variation of the square of the magnetic force is greater than elsewhere, such points will be protected, while if the force is sensibly constant over the surfaces exposed, there will be no protection at any point. With all the forms of experimentation tried this law held without exception. It therefore appears that the particles of magnetic material on which the chemical action could take place are governed by the general law of magnetic attraction and are held in place against chemical energy precisely as they would be held against purely mechanical force. To sum up:-

When the magnetic metals are exposed to chemical action in a magnetic field, such action is decreased or arrested at any points where the rate of variation of the square of the mag-

netic force tends towards a maximum.

It is quite clear that the above law expresses the facts thus far obtained, and while in any given case the action of the magnet is often complicated by subsidiary effects due to currents or bye-products, the mechanical laws of motion of particles in a magnetic field hold here as elsewhere, and cause the chemical action to be confined to those points where the

magnetic force is comparatively uniform.

The effect of currents set up in the liquid during the action of the magnet cannot be disregarded, especially in such experiments as those of Nichols ('American Journal of Science,' vol. iii. pp. 131, 272), where the material acted on was powdered iron and the disturbances produced by the magnet would be particularly potent. The recent experiments of Colardeau (Journal de Physique, March 1887), while perhaps neglecting

the question of direct protection of the poles, have furnished additional proof of the purely mechanical action of the magnet by reproducing some of the characteristic phenomena where chemical action was eliminated and the only forces acting

were the ordinary magnetic attractions.

An attempt was made to reverse the magnetic action, *i. e.* to deposit iron in a magnetic field and increase its deposition where there was a sharp pole immediately behind the plate on which the iron was being deposited. This attempt failed. The action was very irregular and the results not decisive. The question of stirring-effect was also examined. Usually stirring the liquid about one pole increased the action on that pole, but sometimes produced little effect or even decreased it. This, however, is in entire agreement with the irregular action sometimes observed in the case of the after-effect in the original experiments.

An excellent method of experiment is to imbed an iron point in wax leaving the minute point exposed: imbed a flat plate also in wax and expose a point in its centre. Place the point opposite to the plate, but not too near, and place in the liquid between the poles of a magnet and attach to the galva-

nometer as before.

There is a wide field for experiment in the direction indicated above, for it is certainly very curious that the effect varies so much. If hydrogen were as magnetic as iron, of course acids which liberated it would have no action. But it is useless to theorize blindly without further experiment, and we are drawn

off by other fields of research.

In the 'American Journal of Science' for 1886, p. 372, Professor E. L. Nichols has investigated the action of acids on iron in a magnetic field. He remarks that the solution of iron in a magnetic field is the same as removing it to an infinite distance, and hence the amount of heat generated by the reaction should differ when this takes place within or without the magnetic field. Had he calculated this amount of heat due to the work of withdrawing it from the field, he would probably have found his method of experiment entirely too rough to show the difference, for it must be very small. He has not given the data, however, for us to make the calculation. The results of the experiments were very inconclusive as to whether there was greater or less heat generated in the field than without.

In the same Journal, for December 1887, he describes experiments on the action of the magnet on the passive state of iron in the magnetic field. In a note to this paper, and in another paper in the 'American Journal of Science' for April

1888, he describes an experiment similar to the one in this paper, but without our theory with regard to the action of points. Indeed, he states that the ends of his bars acted like zinc, while the middle was like platinum, a conclusion directly the opposite of ours. The reason of this difference has been shown in this paper to be probably due to the currents set up in the liquid by the reaction of the magnet and the electric

currents in the liquid.

In conclusion, we may remark that our results differ from those of Professor Nichols in this: firstly, we have given the exact mathematical theory of the action and have confirmed it by our experiments, having studied and avoided many sources of error, while Professor Nichols gives no theory, and does not notice the action of points; secondly, our experiments give a protective action to the points and ends of bars, while Professor Nichols thinks the reverse holds, and that these are more easily dissolved than unmagnetized iron.

#### XIV. On some Effects of Lightning. By Charles Tomlinson, F.R.S.\*

IN the course of last May and June several letters appeared in the 'Times' newspaper, describing some remarkable effects of lightning. These letters were inserted under such headings as "Eccentricities," or "Vagaries of Lightning;" but it is not difficult for an electrician to assign the effects described to admitted principles, or at least to well-known electrical behaviour.

I have been interested in the subject from the time, nearly half a century ago, when I acted as Snow Harris's scientific representative (as Faraday named me), while that distinguished electrician was getting up his case in defence of his system of lightning-conductors for the British navy. It was my business to search the scientific journals, English and foreign, logs of ships, &c., for cases of damage by lightning. Hence I became tolerably familiar with the "vagaries of lightning," and I find that the cases recorded of late years are not distinguished by any particular novelty. But the lightning stroke is so powerful and irresistible in its effects, that the ordinary observer cannot help seeing many things which, being new to him, he thinks worthy of description in the newspaper. Even medical men sometimes describe cases as novel which are well known to the electrician. Some years ago the frequent accidents that occur to persons seeking refuge from a thunderstorm under a

<sup>\*</sup> Communicated by the Author.

tree were described as having an exact portrait of the tree impressed (or photographed, according to M. Poey) on the body of the victim, whether man or beast. In 1861 I succeeded in transferring to a plate of glass an impress of the discharge of a Leyden jar in all its minute details, consisting of a main trunk (in some cases bifurcated and even trifurcated), branches, and spray. I exhibited these results before the Physical Section of the British Association at Manchester in 1861, and the Astronomer Royal, who presided, remarked that any one of my figures would pass for a tree all the world over. In 1866 an account of a lightning stroke "with an exact portrait of the tree on the body of the victim" appeared in the 'Times.' A letter of mine in that paper on the 10th of September explained how the ramified marks on the body of the victim were impressed by the fiery hand of the lightning without any reference to the tree. Since that time many similar cases have been recorded (in one case the tree-like marks were photographed) and the correct explanation has been given\*.

In some recent cases great surprise has been expressed that, in a row of human beings or animals struck by lightning, the first and the last were the victims, while the intermediate ones escaped. Many such cases are recorded. A file of thirtytwo horses in a stable at Rambouillet was struck by lightning; the first was killed and the last severely wounded. The intermediate thirty were only thrown down. Five children sitting on the same form at school, at Knonau in Switzerland, were struck; the first and the last were killed, but the other three escaped with a shock. In a line of conducting matter of whatever material, the damage, if any, is where the lightning enters and quits the conductor; the intermediate bodies only transmit the charge. Thus, a rod of metal acting as a conductor may be fused at the two extremities. With more imperfect conductors, such as the bodies of animals, there is a greater resistance than in metal; but any resistance in the passage of the charge from one set of more or less perfect conductors to another set may occasion some delay, and any delay, even of a small fraction of a second, allows the heating and expansive force of the lightning to accumulate and so to develop its tremendous effects.

In the cases above referred to, the individuals, whether horses or children, were pretty much under the same conditions. If, however, the conditions are not the same, the

<sup>•</sup> Livingstone, in his 'Missionary Travels and Researches in South Africa,' 1857, says:—"The lightning spread over the sky, forming eight or ten branches at a time, in shape\_exactly like those of a tree."

lightning does not act capriciously, as some suppose, but according to the law of its being. The following case was related to a nephew of mine white Vicar of Denchworth, near Wantage. On June 9, 1832, a woman, Martha Warman, was walking from Wantage in company with two men, she occupying the middle place, when about 1.30 p.m. they were struck by lightning and fell to the ground. The men soon regained their feet, but the woman was dead; her face, body, and clothes were cut and torn, her stockings set on fire, and her boots much rent. But, seeing the curious way in which lightning picks out bits of metal, it must be noted that this woman at the time of the accident was carrying an umbrella, she wore steel in her stays, and had wire in her bonnet, which was fused and twisted. A cross by the wayside marks the

spot.

In this case the metal carried by the woman assisted in forming a line of least resistance, and determining the main trunk of the discharge, while subsidiary branches struck the men with less effect. Hence this case does not disturb the general rule that, when a row of persons or animals is struck, the two outer individuals suffer most. Thus, a miller near Chartres was walking between a horse and a mule. animals were struck and killed. The man's hat was burnt and his hair singed, but he suffered no other injury. On the other hand, when animals are not in a row the effects vary. For example, in August 1833, at Crasnoge-Selo, the stable of the officers' school of cavalry was struck by lightning at one corner of the building. The lightning travelled along the iron racks, setting the hay on fire: the horses all fell to the ground, sixteen of them were killed, and two were rendered quite deaf. The lightning entered the head or neck and passed down the forelegs. The sixteen horses were not together in a row, but were scattered up and down the stable, and it was supposed that those only were killed that were in contact with the metal coverings of the racks,

A remarkable case, which looks like an exception to the rule as to animals in a row, occurred in May last, and was communicated to me by Mr. P. Dudgeon, of Cargn, Dumfries, in which he states that on the 19th of that month, during a thunderstorm at Closeburn, about seven miles north of Dumfries, "a man was leading home two horses just taken from the plough; the two horses were killed instantaneously; the man was uninjured by the lightning, but was hurt by one of the horses falling on him. He was leading the horses on the near side of the pair. This is rather against the theory

of the intermediate bodies transmitting the charge."

In communicating this case to the 'Times' newspaper of June 2nd last, I agreed that this theory does not apply to the above case, and referred to the numerous recorded cases of animals being struck while human beings have escaped. M. d'Abbadie mentions a case which occurred in Ethiopia, in which 2000 sheep were killed by a single flash of lightning. In Sacco, in the kingdom of Naples, on August 17, 1858, out of a flock of 140 sheep the lightning killed 120. The shepherd was not touched and the shepherd boy escaped, but a kid which he had in his arms was killed. In June last three bullocks were killed by lightning in Betchworth Park, near Dorking; and in the same month, at Frensham, several cattle were killed by lightning; some boys left to tend them were struck, but not seriously injured. In short, innumerable cases are recorded in which the shepherd, the farmer, and the huntsmen have been spared, while the sheep and cattle, the dogs and the horses, have been killed.

When Snow Harris was planning his system of lightningconductors for the Houses of Parliament, he explained to me the necessity for strongly protecting the ventilating-shaft of the House of Commons. As a coke fire is usually kept burning in this shaft during the session for the purpose of maintaining a ventilating force, a column of hot rarefied air ascends from this shaft to a considerable height, and would probably act as a line of least resistance, and so determine the course of a stroke of lightning. Indeed a case of this kind occurred in August 1887 at Birmingham, where a chimneyshaft 140 feet high was discharging a hot current into the air. During a storm two men sought refuge in a hut at the base of the shaft, which was not furnished with a conductor: the lightning struck the chimney, passed through the hut, and killed the men. The local paper which recorded the accident states that a mark like the impression of a tree was found on the chest of each man, and signs of scorching in other parts.

When a flock of sheep or other animals are huddled together during a storm a similar column of warm rarefied air is produced. In the case described by Mr. Dudgeon, the horses just taken from the plough were very warm, and sent up a steamy rarefied air which acted as a line of least resistance to the disruptive discharge. The man probably did not share in this rarefied air, and so escaped from the lightning only to be injured by the fall of the horse. This view is confirmed by Mr. Dudgeon, who, having read my explanation in the 'Times,' states that such a view seems to be quite reasonable:—"The day was particularly hot and oppressive (thermometer 79° in the shade), so the horses must have been very

warm, and carrying up with the heated air from their bodies a considerable column of moisture."

Mr. Dudgeon has been so good as to send me the particulars of another interesting case, which occurred during a tolerably severe thunderstorm near Castle Douglas, Kirkeudbright, on the 14th of June last. He remarks that "the details given very distinctly point to a discharge from the earth."

In giving the particulars of this case, we have the somewhat rare advantage of quoting the evidence of an intelligent observer, Mr. J. Douglas, the tenant on the farm where the accident happened. Mr. Dudgeon submitted to him a number of questions, which are here given together with the answers:—

QUESTIONS.
Date 14th June, 1888.

- 1. Were the sheep huddled together or separate?
- 2. Were they in the open or under a tree?
- 3. Were there any marks caused by the lightning on the sheep, or on any of them?
- Were any trees near the sheep struck by lightning at the same time?

ANSWERS.

- 1. Six of them were together, but not huddled; four huddled about 5 yards from the nearest of the six; two in another direction, about 10 yards off the six.
- Six immediately under a tree; four below the outer branches of the tree and in the shelter of a hedge; two in shelter of a hedge.
- 3. Six were covered with soil which hindered any mark being seen; most of the others had a straight dark mark up both sides; one had one of the hoofs nearly torn off.
- 4. No.

These answers were supplemented by a letter addressed to Mr. Dudgeon by Mr. Douglas. Premising that a number of sheep were grazing in a field near a small wood to which they had access, the narrative thus proceeds:—

"At the time the storm was at its worst, there was a heavy hail-shower. The sheep being not long clipped, seem to have gone to the trees for shelter. It was under a beech-tree the lightning struck the earth at three places, equally distant round the tree, and about a foot or two from it. It then went in two directions, one at right angles to the other. In one direction it followed one of the roots of the tree, laying bare the soil, and stripping the bark off the root, and killing four sheep in the direct line of it below an oak-tree and an old hedge. In the other direction it cut up the ground until

it came to an oak-tree, which it went half round, grazing the bark, and then continuing the same straight line which it had been following, and killing two sheep, one about two yards in front of the other, both in line. Where it had first struck the ground, it sent the earth and grass to a great height, the leaves of the trees being covered with earth to a height of from fifteen to fifty feet. The earth being washed down by the heavy rain so covered the sheep as to prevent any mark being seen. One of the sheep was bleeding at the mouth, and another had a hoof nearly torn off. The six were lying from one to two yards from each other. A girl who saw them first, and immediately after the stroke, says there was another sheep trying to get up; she assisted it and it ran off. It does not seem to have been injured, but it had the same dark blue mark as the others up each side and across the The tree struck does not look any the worse, nor

any other tree near it."

Certainly, some of the effects described in the above interesting case seem to justify Mr Dudgeon's opinion that the electrical discharge proceeded from the ground upwards. There are recorded cases of this sort, and when these are referred to by Arago, in his celebrated essay "Sur le Tonnerre," contained in the Annuaire pour l'an, 1838, it is with some hesitation. If lightning moves with the velocity attributed to it by Wheatstone, how can we tell whether it ascends or descends? The answer must be, by its effects. This subject was much discussed by the electricians of the last century, in connexion with what the Earl of Stanhope termed "the returning stroke." When a mass of electrified cloud induces an opposite state on the earth's surface, and a disruptive discharge takes place, the neutralization is by no means complete; a portion of the earth's surface returns to its former excited condition together with the dielectric air above it, and another discharge may take place from the ground upwards, and this at a considerable distance from the inducing system of clouds. In a case related by Mr. Brydone (Phil. Trans. 1787) that occurred in Scotland, a cart laden with coals, drawn by two horses, was proceeding along a road, the carter sitting in front of the cart. The lad and the horses were struck dead, although no lightning was observed near the place. There was a storm a long way off, which Mr. Brydone was watching at the time, but within half an hour of the accident he was on the spot. On examining the wheels of the cart, circular holes were found in the ground, immediately under them, about twenty inches in diameter, at which points the iron tires exhibited marks of fusion.

coals also were scattered. The theory of the return stroke is that such effects as the above result from the discharges of the remote clouds producing electrical disturbances in distant bodies, even some miles from the spot over which the

thunder clouds appear.

The case related by Mr. Brydone resembles in several particulars the recent case communicated to me by Mr. Dudgeon. In the one the hair was singed on the legs, and under the bellies of the horses; in the other there were marks of singeing in the regions of the kidneys of the sheep. In both cases the animals were struck suddenly stone dead. Mr. Brydone, who, as we have said, examined the spot soon after the accident, says:—"Had there been any convulsive struggle, the marks would have been visible in the dust of the road where they fell." And, as a further analogy, "a shepherd standing in an adjacent field stated, that he had his eye on the waggon at the very instant of the explosion, and saw a vortex of dust arise." In Mr. Douglas's narrative the soil was hurled upwards so as to cover the leaves of the trees

to a considerable height.

Arago is so sceptical as to the possibility of a lightning discharge from the ground upwards (de bas en haut) that he is disposed to attribute the explosions above described, including the turning up of the soil, and the barking of the roots of the trees, to the conversion of the moisture of the soil into high-pressure steam by the intense heat of the lightning; just as he accounts for a large tree being split up into matches by the conversion of the sap into the same tremendous elastic force. But in the case at Coldstream, Brydone says nothing about rain, and the principal effects occurred in a dusty road. He also describes a very curious case, which supports the idea of a discharge from the ground upwards. A woman who was cutting grass on the banks of the Tweed was suddenly thrown down without any apparent cause. She called her companions immediately to her aid, and told them that she received a sudden and violent blow on the soles of her feet, but whence it proceeded she could not tell. At the moment this happened there was neither thunder nor lightning.

Arago admits that the facts as to ascending lightning are against him, although they do not amount to demonstration. He is also sceptical as to the phenomena of ball lightning (éclairs en boule) or that which moves through the air at a comparatively slow rate, appearing like a luminous ball or a globe of fire. Arago terms this ball lightning a stumbling-block (pierre d'achoppement) for meteorologists, due probably

to an optical illusion. We need not discuss his objections, seeing how numerous the cases are, and, apparently, well established. Let us take only one or two cases. Mr. Chalmers states ('Phil. Trans.' xlvi.) that, being on board the 'Montague '(seventy-four guns) on November 4th, 1749, he observed a large ball of blue fire rolling along on the surface of the water, as big as a millstone, at about three miles dis-Before they could raise the main-tack, the ball had reached within forty yards of the main chains, when it rose perpendicularly, with a fearful explosion, and shattered the main topmast in pieces. So also on the Malvern Hills, in June 1826, a ball of fire was observed to roll along the hill towards a building where some people had taken shelter. Here it exploded, and killed two of them.

According to Snow Harris these luminous balls result from a kind of brush, or glow-discharge. In the case of the 'Montague,' it was rolling on the surface of the water towards the ship from to windward. This was evidently a sort of glow-discharge, or St. Elmo's fire, produced by some of the polarized atmospheric particles yielding up their electricity to the surface of the water. On nearing the ship the point of discharge became transferred to the head of the mast; and the striking distance being thus diminished, the whole system returned to its normal state, that is to say, a disruptive discharge ensued between the sea and the clouds, producing the usual phenomena of thunder and lightning, termed by the observers "the rising of the ball through the mast of the ship." The case on the Malvern Hills is another instance of the same kind.

Arago is particularly sceptical as to the appearance of globular lightning within the walls of a building, but he quotes a case related by Maffei, which occurred in September 1713, in the territory of Massa-Canara, in Italy. He took refuge from a storm in a château, where he was received by the mistress of the house in a room on the ground floor. Suddenly they saw a bluish-white flame rise from the floor, agitated, but with no progressive motion. After gradually acquiring a considerable volume it suddenly disappeared. Maffei felt in his shoulder, proceeding from his back upwards, a peculiar tickling sensation (un chatouillement particulier), plaster detached from the ceiling fell upon his head, and an explosion occurred, which did not resemble the sound of thunder.

A case is recorded in Mr. Symons's Meteorological Magazine for 1883, as having occurred on July 28th, about 6 p.m., in the printing-office of Mr. Burt, Mount Washington, New Hampshire, U.S. Mr. Burt says:—"I saw a ball of fire as large as a man's head in front of me, not three feet off. It exploded with a tremendous noise. My left leg seemed to be completely paralysed, and I fell to the floor. Three of my printers were in the room at the time, two sitting at the table near me, and one standing up a little further off. The latter had the skin of one hand torn, another was hit in the back, and the third escaped without injury." A tree-like mark was found on Mr. Burt's back.

This seems also to be a case of glow-discharge passing into

an ordinary disruptive discharge.

We trust the readers of the Philosophical Magazine will excuse the elementary nature of the foregoing details; but it seems to be necessary that Science should sometimes lift up her voice to point out how so many of the effects of lightning which every year are described in the newspapers as unusual, eccentric, &c., are ordinary events to be explained on well-known principles.

Highgate, N., July 6, 1888.

XV. Note on some Additions to the Kew Magnetometer. By T. E. Thorpe, Ph.D., F.R.S., and A. W. Rücker, M.A., F.R.S.\*

IN making field observations with the Kew magnetometer it is important that the mirror by which the image of the sun is formed should either be in perfect adjustment, or that

the errors should be known and allowed for.

The axis about which it rotates is made horizontal by means of a riding level. The plane of the mirror is made parallel to the axis by adjusting it until the image of the cross wires formed by reflexion in the mirror does not alter its position when the mirror is inverted in its bearings. The axis of the mirror is made perpendicular to the optic axis of the telescope by making the cross wires and their image coincident. In the course of the Magnetic Survey of Great Britain and Ireland, on which we have been for some time engaged, we have found such great difficulty in making these adjustments in the field, that we have for a long time practically abandoned this method, and adjusted the mirror from time to time, either indoors by means of a plumb-line, or by observations on some convenient object external to the instrument in the field. have always, when possible, made four sets of sun observations, reversing the mirror in its bearings, and taking "front"

<sup>\*</sup> Communicated by the Physical Society: read June 9, 1888.

and "back" views, in which the observer looks towards the sun and stands with his back to it respectively. We have thus been able to eliminate the errors of adjustment of the mirror, and to assure ourselves that each observation was

satisfactory.

This method is, however, open to some objection. When the sky is cloudy it may be impossible to see the sun for a time sufficient to take all four sets of observations. On such occasions we always pay special attention to the adjustment of the mirror, but it may happen that no object near the station is sufficiently elevated to be used for the purposes of correction. In that case it is necessary to rely on the result of a long experience, which proves that if reasonable care is taken of the instrument the mirror does not get seriously out of adjustment during a journey by road or rail extending over a day or two.

Nevertheless, there can be no doubt that the method of correcting by the image of the cross wires has the advantage that it can, theoretically at all events, be carried out at the

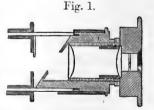
place and time at which the observations are made.

The practical drawback which led us to abandon it was the difficulty of seeing the image of the wires. In the neighbourhood of the cross wires the metal of the telescope tube is cut away, but the light thus admitted is insufficient. On a gloomy day, when the sun was only visible at rare intervals, and when, therefore, it was most important that the mirror should be in order, the necessary adjustments could not be made. Even on a bright day it was desirable to envelop the observer's head and the instrument in a dark cloth, and this was difficult and troublesome if the wind was high.

We have, therefore, lately devised some additions to the magnetometer which, although extremely simple, make it practically possible to use the cross wires for making the

adjustments.

A polished platinum mirroris introduced into the telescope between the eye-piece and the cross wires, which are viewed through a hole in its centre. The mirror is inclined at 45° to the axis of the telescope, and reflects a considerable quantity of light upon the wires.



A bronzed brass tube is attached to a support which fits into the three holes which are provided to fix the magnet-box in position. This tube extends from the telescope to the mirror, and thus shuts out extraneous light. It can be packed in the ordinary magnetometer-box, and when it is in position, and the platinum mirror is directed towards the sky, or, if desirable, towards its brightest part, the image of the wires can readily be seen. If the background reflects much light, it is desirable to place a small blackened metal screen weighted with lead on the horizontal circle which carries the mirror. This can be lifted off without in any way interfering with the adjustments.

The following two examples may serve to indicate the degree of precision with which the adjustment of the mirror

can be made.

Observations were taken both when the observer was looking towards and directly away from the sun. The N point on the circle is deduced from the front observations. The collimation correction is obtained by combining the front and back observations. It will be seen that the uncorrected results are quite as good as those to which the collimation correction has been applied, which proves that the mirror can be adjusted to within the limits of the error of observation on the sun.

Station.	G. M. T.	Altitude of Sun.		Collimation correction.	Corrected N point.
Horsham. (April 21, 1888.)	h. m. s. 12 43 49 15 15 44 17 4 0	50 2.2 34 33.7 18 12.7	297 4·2 297 3·8 297 3·6	+0°·3 -0·6 -0·1	297 4·5 297 3·2 297 3·5
Alresford. (April 28, 1888.)	14 10 36 15 45 6	45 7.8	241 23·0 241 22·5	-0·1	241 22·9 ermined.

In cases where it is for any reason impossible to take the back observations, or if the sun is so frequently covered that it is advisable to observe without waiting to adjust the mirror, it is advantageous to be able to determine how much error has been introduced. For this purpose we have placed in the plane of

the cross wires a fine scale engraved on ivory. The angular deviation of the mirror which produces a given displacement of the image of the cross wires on this scale can be determined, and when this is known the error of the mirror can, on any subsequent occasion, be deduced from the deviation of the image.



The following observations were made in a lofty room on an object the elevation of which was 40°:—

Scale Reading of Image of Cross Wires (x).	Reading on Circle $(\rho)$ .	$x-x_0$ .	$\rho - \rho_0$
-5.65	$2\overset{\circ}{6}4$ $4\overset{\circ}{2}\cdot 1$	-5.45	6.4
-3.60	264 39.5	-3.40	3.8
-0.20	264 35.7		
+2.80	264 32.6	3.00	-3.1
+5.45	264 29.0	5.65	-6.7

All the readings are the mean of two which differed but little, and between which the axle of the mirror was inverted in its bearings. Hence if  $\alpha$  be the angular value of a scale-division, *i.e.* the error of collimation of the mirror which corresponds to a displacement of the image through one division,

$$\rho - \rho_0 = \frac{2(x - x_0) \alpha \sin^2 20^\circ}{\cos 40^\circ}$$
$$= 0.306 (x - x_0) \alpha,$$

We thus get four values of  $\alpha$ , viz. 3'·8, 3'·7, 3'·4, and 3'·9, the mean of which, viz. 3'·7, may be taken as correct.

To check this value, observations were made at South Kensington on the sun, and on a pinnacle of the Natural History Museum, both when the mirror was in good and when it was in bad adjustment. It will be seen that the corrected values are in close accord.

Thus on May 9th, at 12<sup>h</sup> 46<sup>m</sup> 36<sup>s</sup>, when the altitude of the sun was 54° 39'.8, the N point on the scale was found to be 58° 11'.2. The mirror was then thrown out of adjustment, the mean reading for the image of the cross wires being +5.7 div. Another observation on the sun was made at 1<sup>h</sup> 13<sup>m</sup> 12<sup>s</sup>, when the altitude was 52° 51'.5, which gave for the reading of the north point 57° 56'.9.

The correction is

$$\frac{2 \times 5.7 \times 3.7 \sin^2 26^{\circ} 26'}{\cos 52^{\circ} 51'} = 13'.8.$$

Hence

$$57^{\circ} 56' \cdot 9 + 13' \cdot 8 = 58^{\circ} 10' \cdot 7$$
,

which differs only by half a minute from the value obtained

when the mirror was in adjustment.

In like manner the bearing of a pinnacle, as given by the mirror in adjustment, was 128° 40′ 8, while, when the reading for the image of the cross wires was +5.7 div., it was.

$$128^{\circ} 40' \cdot 2 + 0' \cdot 8 = 128^{\circ} 41' \cdot 0.$$

The elevation was  $15^{\circ}$  39', and the two results agree to  $0'\cdot 2$ . It is evident from these test cases that, since the error of the mirror was far larger than that produced by travelling for a day or two, observations in the field can, by means of the scale, be corrected to within the limits of the error of experiment.

The additions to the magnetometer, which we have here described, were made for us by Messrs. Elliott, and we venture to think that they might with advantage be incorpo-

rated in standard instruments of the Kew pattern.

XVI. Experiments on Electrolysis.—Part II. Irreciprocal Conduction. By W. W. Haldane Gee, B.Sc., Lecturer of the Victoria University, and H. Holden, B.Sc., Bishop Berkeley Fellow in Physics, of the Owens College, Manchester\*.

#### [Plate I.]

WE have observed, when strong sulphuric acid is used as an electrolyte, the electrodes being of platinum, that the decomposition nearly ceases, if by decreasing the resistance in circuit we attempt to increase the current beyond a certain maximum. An investigation of this curious behaviour has shown that it may best be included with the miscellaneous phenomena grouped under the head of unipolar, or, as it may better be called, irreciprocal conduction †. The early experimenters in voltaic electricity devoted much attention to this subject, and it will be desirable to give some

\* Communicated by the Physical Society; read 26th May, 1888. This is the second of a series of papers on Electrolysis and Electrolytic Polarization, descriptive of experiments made since January 1887 at the Owens College Physical Laboratory. An abstract of the experiments made, to the end of August 1887, was submitted to the British Association meeting at Manchester. We desire to acknowledge the assistance received up to that time from Mr. C. H. Lees, B.Sc., Derby Mathematical Scholar of the Owens College. His cooperation has since been discon-

tinued, owing to absence at Strasburg.

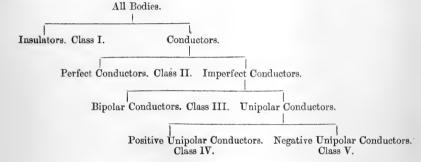
† Following Christiani's use of the term, irreciprocal conduction is said to occur if a reversal of the direction of a current causes any change in its magnitude,

account of their labours before proceeding to describe our own experiments.

#### Section A. HISTORICAL AND CRITICAL.

### 1. Experiments of Erman.

Among the many papers in the earlier volumes of Gilbert's Annalen der Physik, which the invention of the voltaic pile had directly inspired, will be found several by Prof. Erman of Berlin. With the aid of the imperfect instruments known at that time he made an investigation on the conducting power of bodies; and in his fourth research\* there appears a division of bodies into five classes, of which the following schema shows the chief features:—



To understand this classification it will be necessary to describe the method of experiment employed by Erman in order to find the class to which a body belonged. PN (fig. 1) is a well insulated Volta's pile, P and N being the positive and negative poles respectively. Connected with P is a goldleaf electroscope  $E_p$ , and with N a similar electroscope  $E_n$ . The body (B) to be tested, which is permanently connected with earth, is made to touch separately  $E_n$  and  $E_n$ . If the body belongs to Class I. neither of the electroscopes will be affected, but the case is otherwise if B is a conductor. Let us suppose the latter; it will, therefore, be necessary to ascertain to which of the other four classes the body belongs. Permanent connexions are made (as represented by the dotted lines of fig. 1) with B, and the behaviour of the electroscopes is carefully noted. If there is a sudden and complete collapse of the leaves of both E, and E, the

<sup>\* &</sup>quot;Ueber die fünffache Verschiedenheit der Körper in Rücksicht auf galvanisches Leitungsvermögen." Gilbert's *Annalen der Physik*, Band xxii. S. 14 (1806).

body belongs to Class II.\*; if, on the other hand, both  $E_p$ , and  $E_n$  are partially discharged, B is placed in Class III. If  $E_p$  alone is discharged, B is a positive unipolar conductor; if this is the case only with  $E_n$ , B is a negative unipolar conductor.

At the time when Erman classified conductors in this manner Ohm's law was not known, hence the behaviour of the electroscopes under these conditions could not be thoroughly appreciated. However, it was recognized that in the cases of Classes IV. and V. there must be a high resistance at one of the contact points n or p, preventing the conduction of the charge of  $E_n$  or  $E_p$  to earth.

It was found that well-dried soap was a good example of Class V. Hence Erman studied the unipolar conducting-power of soap in some detail, but he was unable to come to any definite conclusion why at p there should be a very high resistance. He rejected, on grounds which need not here be described, the hypothesis of an insulating film composed of

the decomposed soap-acids †.

Interesting examples of Class IV., Erman found, are furnished by flames. Their anomalous conductivity yet remains but imperfectly explained ‡.

# 2. Experiments of Ohm. (a) On Soap.

Ohm § confirmed the experiments of Erman, and came to the conclusion that the cause of the high resistance at the anode was due to a layer of fatty acids.

- \* The following extract from Erman's paper (loc. cit. p. 18) is interesting, as evidence of his scientific caution:—"The distinction between perfect insulators and perfect conductors was perceived very early with the battery, and though it may indeed be believed that no important discoveries remain to be made in this matter, it is very desirable not to consider the matter as fully settled, for it is possible that also here important modifications of conductivity lie hidden. For example, it has really not yet been proved whether, with the so-called perfect conductors, there are not degrees of conductivity. Thus, though it is usual to regard all metals as equally good conductors, I should like this law not to be so unconditionally assumed, before direct measurements have proved its generality. Indeed, who knows whether finally with each metal certain properties will not be made apparent, which in respect to galvanic electricity are analogous to those which so excellently characterize iron, nickel, and cobalt with regard to magnetism?"
- † Loc. cit. p. 50. ‡ The conducting power of flames has been studied by Ritter, Hittorf, Andrews, Hankel, Braun, Fuchs, Macfarlane, Rintoul, and others.

Schweigger's Journal, lix. (1830) p. 385.

# (b) On Sulphuric Acid and Caustic Potash.

Ohm\* employed a galvanometer in studying the unipolar conductivity of these liquids. The instrument was placed in series with 1-6 single fluid zinc-copper cells, and a voltameter containing strong sulphuric acid. Employing electrodes of platinum, gold, silver, copper, iron, lead, and tin, he found that the deflection obtained on first making the circuit speedily sank to a very small amount. He showed that the cause diminishing the current was between the anode and the acid; for on bridging across the anode and the liquid by some moist threads the deflection was immediately increased to the original amount. Also, in the case of the oxidizable metals, by diluting the liquid in the neighbourhood of the anode the current was greatly increased, whilst a dilution of the liquid near the kathode produced no effect. Further, replacement of the anode by a clean electrode produced the original deflection for a time, whilst changing the kathode made no difference. He finally concludes that the fall of the current is due to the development of a force at the anode. This conclusion he verified by the use of an electroscope. strong sulphuric acid is classed amongst the negative unipolar conductors t.

Ohm also experimented with various electrodes in strong potash solution, which led him to regard the latter as a positive unipolar conductor.

# 3. Experiments and Theory of Christiani.

The only modern contribution of importance to the subject of irreciprocal conduction is the pamphlet ‡ produced by the late Prof. Christiani, whilst working in the laboratory of Du Bois Raymond. He investigated generally the case of electrolysis with unequal-sized electrodes, and comes to the conclusion that, as a rule, with low E.M.F.'s the current is able to

\* Schweigger's Journal, lx. (1830) p. 32.

† It seems probable that what Ohm observed was a decrease of current due—(1) in the case of the oxidizable electrodes to a transition resistance caused by the formation of a badly conducting salt-layer on the anode in strong sulphuric acid; (2) in the case of platinum and gold in sulphuric acid and potash solution to polarization, this polarization being of a unipolar nature, that is to say it was much greater at one electrode than at the other. We do not believe that Ohm ever observed the phenomenon of unipolarity in strong sulphuric acid with electrodes of platinum or gold due to a transition resistance. This conclusion is supported by comparing Wiedemann, Electricität, Band ii. pp. 629, 657.

‡ Ueber irreciproke Leitung electrischer Ströme. Berlin: Friedländer

und Sohn (1876). Contains 174 pages and 15 plates.

pass more easily from the lesser to the greater electrode, and vice versâ with large E.M.F.'s. This difference, he says, exists after the influences of polarization and chemical transition resistance are allowed for, meaning by the latter term a resistance due to the products of electrolysis. We have been at some trouble to examine the experiments and reasoning upon which the above conclusion is based, and have arrived at the opinion that they are equally open to criticism; his results and theory being, however, very interesting and representing a large amount of work, it will hence be desirable to notice them at some length, especially as his pamphlet is not readily accessible in England.

In order to eliminate as much as possible changes in the electrolyte caused by the passage of the current, momentary currents from an induction-coil were used throughout the greater part of his work, his object being a study of the nature and causes of irreciprocal conduction, with unequal-sized electrodes, in electrolytes. For this purpose, applying a momentary E.M.F. to the voltameter, he desires to measure:—

(a) The quantity of electricity which is sent through the voltameter by this E.M.F., and (b) the polarization which

opposes its passage.

Fig. 2 shows the essential parts of the arrangement used with induced currents. V is the voltameter with a platinum plate and a platinum Wollaston's point as electrodes. In circuit with it are a dead-beat Wiedemann's galvanometer (G) and the secondary coil (S) of an induction-coil, of which P is the primary coil in circuit with a battery. By changing the distance of S from P(=x), the E.M.F. of the induced current can be varied. The experiments were conducted somewhat as follows:—By opening the primary circuit a quantity of electricity  $(=q_1)$  is sent through the voltameter, and the kick  $(=k_1)$  on G is noted. If the deflection does not return exactly to zero, but goes on the other side of it, this negative deflection  $(=e_1)$  is observed, and afterwards, in discussing the possible causes of irreciprocal conduction, is taken as a measure of the polarization opposing the passage of  $q_1$ . The same induced E.M.F. is now, by reversing the voltameter terminals, applied in the opposite direction. Let  $k_2$  and  $e_3$ be the deflections now obtained, and suppose that  $q_2$  is the quantity of electricity sent through the voltameter in this direction of the current. The distance of S from P is now altered, generally by 5 millim. at a time, and at each new position the above procedure is repeated, giving values of  $k_1$ and  $k_2$  for each value of x. He finds that  $k_1$  and  $k_2$  are enerally different, but for one value of x they are equal; for

values of x below this, one of them is the greater; for values of x above this, the other is the greater. He then assumes that  $k_1$  and  $k_2$  are proportional to  $q_1$  and  $q_2$  respectively, and

thus proves the existence of irreciprocal conduction.

The assumptions made, namely (1) that  $e_1$  is a measure of the polarization E.M.F. which opposes the passage of  $q_1$ , and (2) that  $k_1$  is exactly proportional to  $q_1$ , do not seem to be admissible. Firstly, with regard to (1), e1 is really proportional to the depolarization current which exists a certain time, conditioned by the time of vibration of the galvanometer &c., after the charging E.M.F. has ceased, and is not proportional to the value of the polarization E.M.F. during the existence of the charging E.M.F., unless the rate of depolarization is constant, which it usually is not. Also, as will be shown in a subsequent paper, the rate of depolarization with unequal-sized electrodes depends on the direction of the charging current. It may also be noticed that  $q_1$  or  $q_2$  &c. do not necessarily bear any simple relation to the value of the induced E.M.F. The quantity of electricity which passes in any time dt during the existence of the induced E.M.F. is proportional to the difference between the values at that time of the induced E.M.F. and of the polarization; and therefore the relation between the charging E.M.F. and the quantity of electricity which passes during its existence depends on the rate of increase of the polarization E.M.F., which can scarcely be said to be known, but is probably not constant, and may even vary according to the direction of the current. validity of assumption (2) is also doubtful, for the kick (k) on the galvanometer depends not only on q (the quantity of electricity which passes during the existence of the induced E.M.F.) but also on the magnitude of the depolarization current, since the duration of the induced E.M.F. is certainly over before the galvanometer-needle has moved from zero to kThus it would seem that k is only at best, in the case of non-polarizable electrodes, an approximation to the value of q; and therefore Christiani's numbers are not sufficiently trustworthy to serve as foundation for an elaborate

Christiani, however, assumes that k and q are exactly proportional and plots curves \* giving the relation between q and the induced E.M.F. in the two directions of the current. The point of intersection of the two curves is called the reciprocal point; its abscissa being proportional to the induced E.M.F.,

These curves are regular and never intersect in more than one point, and with some electrolytes do not intersect within the limits of experiment.

which gives equal kicks in the two directions, and its ordinate equal to these kicks. The conditions for the occurrence of reciprocity are then investigated. He finds (1) that lessening the size of the point electrode causes reciprocity to occur with lower E.M.F.'s, but that fairly large changes in the size of the plate electrode or in the distance of the electrodes have not much influence; (2) that decreasing the temperature causes reciprocity to occur with lower E.M.F.'s; and (3) that the degree of concentration of the solution is of influence. A discussion of the possible causes of irreciprocal conduction follows. Polarization, he says, cannot be the cause of irreciprocity, because he has obtained the latter with non-polarizable electrodes. Further, some measurements of the polarization by a wippe method show, as far as such a method is satisfactory\*, that polarization is not the main cause of irreciprocity. His arguments against polarization, based on the measurements of  $e_1$  (see p. 130) are, as before explained, of no value. His main argument against a chemical transition resistance is the following experiment:—A solution of potassium iodide is taken, and a certain number of currents sent through until the E.M.F. is found for which reciprocity occurs; the electrodes are then taken out and cleaned, and fresh solution used. The same E.M.F. is now again applied, and it is found that reciprocity still occurs; or, in other words, changes in the electrolyte caused by the passage of previous currents do not affect the value of the E.M.F., for which the momentary currents are the same in the two directions. The direction in which the E.M.F. is first applied is also quite indifferent. He remarks, however, that the reciprocal point in other electrolytes is, to some extent, affected by the passage of previous currents.

Christiani to a small extent makes use of permanent currents, but only in the case of the so-called non-polarizable electrodes. The following specimen of his results, with amalgamated zinc electrodes in concentrated zinc sulphate, will indicate their general features:—

<sup>\*</sup> The values of the polarization obtained by this method are of course open to the objection that they depend on the rate of fall of polarization after the removal of the charging battery.

1st Experiment.—Plate electrode =  $P_p = 37 \times 26$  millim. Point electrode =  $P_s = \frac{1}{2}$  size of  $P_p$ .

Seconds after	Deflections.		
making circuit.	$P_s+.$	P <sub>8</sub>	
0	217	217.5	
120	Begins to fall.		
600	45, vibrating.	220	

2nd Experiment.— $P_p$ =same size as before.  $P_s = \frac{1}{4}$  size of  $P_p$ .

Seconds after	Deflections.			
making circuit.	$P_s$ +.	Ре		
0	188.0	196.0		
40	Begins to fall.			
180	14.0, vibrating.			
600		196.0		

Here it seems evident that the irreciprocity is due to the gradual formation of a badly-conducting film on the anode, but Christiani does not accept this simple explanation, apparently because it would not, as he thinks, explain the results obtained with transient currents.

Having rejected both polarization and a chemical transition resistance as causes for the effects obtained, a theory of electrolysis which would afford an explanation of them was necessary. The theory which Christiani evolves is a direct development of the idea that electrolysis is a convection of electricity by the atoms of matter. He considers the mechanism of electrolysis to consist in the two ions of a molecule conveying equal and opposite quantities of electricity in opposite directions, but assumes (1) that the impulse causing this motion takes place only at the anode. He assumes, moreover, (2) that in a given electrolyte the number of atoms (=n) which meet any unit area in unit time only depends

on the temperature of the electrolyte. Finally, he makes use of the assumption (3) that every monad ion carries the same quantity of electricity (=e). These assumptions are applied finally to the case of unequal-sized electrodes, a plate of area P and a point of area S, as follows. According to assumption (2) the number of atoms which touch the plate in unit time will be nP, and therefore by (3) the greatest quantity of electricity which can leave the plate by ordinary convection in unit time is nPe, and similarly nSe is the greatest quantity of electricity which can leave the point in unit time. He then argues that, although n is a very large quantity, e is a very small one, and that it may thus happen that nPe and nSe are quantities of electricity small enough to be dealt with in experiment. He then considers the effect of an E.M.F. (=E)acting in the circuit for a very short time (=t). Suppose that the plate is the anode and let such an E.M.F.  $(=E_n)$  be applied for a very short time (=t) that the quantity of electricity which passes is equal to nPet. In this case, when the E.M.F. applied is just sufficient to charge the nPt atoms which appear at the plate anode during the time t of charge, Christiani says, from energy considerations, that the most favourable conditions for the passage of the electricity are attained, or, in other words, the resistance of the cell is now a minimum. If the E.M.F. applied be less than  $E_p$  the resistance of the cell increases because all the atoms which touch the anode are not engaged in carrying the electricity; if, on the other hand, an E.M.F. greater than  $E_p$  is used, the resistance of the cell again increases because a process analogous to spark-discharge has to go on. Similarly, if the point is the anode, there will be a certain E.M.F.  $(=E_s^t)$  for which the resistance of the cell,

for the direction of the current, is a minimum  $\left(=\frac{E_s}{nSe}\right)$ . Let the E.M.F. actually applied be E, there are then three cases possible. Since  $E_s < E_n$ ,

(1) 
$$E < E_s < E_p$$
, (2)  $E_s < E < E_p$ , (3)  $E_s < E_p < E$ .

Now, according to Christiani, the resistance of the cell is greater or less (i.e. an additional electrical transition resistance is greater or less) according as the E.M.F. applied is more or less different in value from that giving the minimum resistance. Thus in case (1), where E is nearer to  $E_s$ , the quantity of electricity which passes will be greater if the point is the anode. In case (2), where E is between  $E_s$  and  $E_p$ , there will be one value of E which will give equal quantities of electricity in either direction of E. In case (3), where E is

nearer to  $\mathbf{E}_p$ , the quantity of electricity will be greater if the

plate is the anode.

The theory is thus highly ingenious, but its verification is a matter of considerable difficulty, for we have to distinguish the effects of polarization and *chemical* transition resistance from the *electrical* transition resistance. As we have pointed out, Christiani's own results are open to doubt, so that unless some better method of experiment can be suggested the hypothesis of Christiani must remain but an interesting speculation.

#### Section B. DESCRIPTIVE OF OUR EXPERIMENTAL WORK.

## 1. Arrangement of Apparatus.

We have found the arrangement shown in fig. 3 very convenient for the larger part of our experimental work.

M is a battery consisting usually of from 1 to 6 secondary

cells;

 $k_1$  is a commutator for reversing the main current;

k<sub>2</sub> is a four-way plug-key enabling the voltameter-circuit to be broken or short-circuited, or cut out of the circuit altogether;

V is the electrolytic cell;

G is a dead-beat Deprez and D'Arsonval galvanometer;  $k_3$  is a commutator used to reverse the current through G;

 $k_4$  is a switch hinged at E. According as the contacts D and A or those at C and B are made, then (1) the battery is included or excluded from the voltameter-circuit, (2) the low-resistance galvanometer-shunt  $S_p$  or the high resistance galvanometer-shunt  $S_s$  is in use, and (3) the resistance-box  $R_p$  or  $R_s$  is employed. The switch  $k_4$  enables us, therefore, to study the changes of current-intensity when the electrolytic cell is in circuit with the battery, and also the changes of the polarization-current which ensue after cutting the battery out of the circuit.

#### 2. Experiments with strong H<sub>2</sub>SO<sub>4</sub> and Pt Electrodes.

a. General description of the Phenomenon to be observed.— In the opening paragraph of this paper it was stated that, through a given voltameter, consisting of Pt electrodes in strong H<sub>2</sub>SO<sub>4</sub>, currents of an intensity below a certain maximum could alone pass, and that if we tried to increase the current strength above this maximum, it was found that the deflection on a galvanometer in circuit diminished nearly to zero, and that decomposition nearly ceased. Further investigation soon showed that the size of the electrodes was also of great influence in determining the stoppage of the current, as is well shown by the following arrangement (see also Table I.). Take two clean platinum electrodes, one being much larger than the other, and place them in strong pure H.SO4. It will be found that a very large current can pass from the larger to the smaller electrode (see fig. 4, a direction of current), giving a deflection say of several hundred divisions on the galvanometer. On reversing the current (see fig. 5,  $\beta$  direction of current), if it be of suitable strength, after the first sudden deflection the galvanometer-needle will soon return nearly to zero; in many cases scarcely a trace of a deflection is to be observed; in fact the current in the a direction may be more than a thousand times as great as that obtained in the  $\beta$  direction on reversing  $k_1$ . We desire to ascertain the cause of this (almost total) stoppage of the current, and to study generally the conditions determining its occurrence; and in connexion with this, it may be noted that the formation of a sheath of gaseous bubbles round the anode always attends this stoppage of the current with Pt electrodes.

b. Experiments proving Existence and Locality of an Insulating Film.—If, after the production of the insulating condition, we replace the kathode by a large electrode the current is still stopped, but if the anode be similarly exchanged the current passes readily. This experiment proves that there is some obstructing cause at the anode. To determine its nature attempts have been made to measure the polarization and resistance of the cell in the  $\alpha$  and  $\beta$  directions. Operating very rapidly with the dead-beat galvanometer, and using Ohm's method, we find that the resistance in the  $\beta$  direction (after the insulating condition is produced) is very much greater than in the  $\alpha$  direction. Thus in one experiment the resistance in the a direction was only 10 ohms, whereas on reversal it rose to 10,000 ohms, and continued to increase for some time after the insulating condition was produced. The polarization, on the other hand, may be regarded as equal in the two directions, for, using a compensation method in which the voltameter-circuit was momentarily opened, and the polarization balanced against a known E.M.F., we have found 2.5 volts to be the value both when the insulating condition was produced, and also when it was not. This result was confirmed by Ohm's method. Thus the polarization is not abnormal, and therefore cannot be a determining factor in producing the insulating condition. Such a conclusion was from the first to be expected, as the stoppage of the current had been produced when a battery having an E.M.F. of ten

volts and upwards had been employed. Measurements of the resistance were also taken by Kohlrausch's method, this being done by breaking the circuit of fig. 3 between a and b, and including the arrangement in one of the arms of a Wheatstone's bridge. It was found very difficult to get anything but a very approximate value of the resistance during the insulating condition, for the passage of the alternate currents apparently tended to destroy the insulation, and caused continual vibration of the needle of the dead-beat galvanometer. This effect was much less when the current was sent in one direction through the primary coil of the induction-coil than The values of the resistance obtained, however, in the other. fully confirmed those obtained by other methods; so that we may conclude that the insulating condition is due to a resistance at the anode. In what follows it will be convenient to regard this as due to a film of badly-conducting matter.

c. The Film-forming Current-density.—If we increase the size of the anode a greater current is necessary to produce the insulating condition, hence the current-density at the anode is an important factor in determining the formation of the film (see Table I.). Calling C the minimum current which will form the film and S the whole surface of the anode immersed, then  $C/S = \Delta$  we shall define as the film-forming current-density. The actual value of  $\Delta$  depends upon several conditions, such as will be best understood after an examina-

tion of Tables I. and II.

Examination of the following and similar observations show that  $\Delta$  is not perfectly definite in value, but is greatly influenced by the previous treatment of the anode. For example, if the anode has been heated to redness and washed before putting in the current, the film forms with a less value of  $\Delta$ than if the anode had been previously used for electrolysis (see experiments 2 and 3, Table I., and 5, 6, 7, and 21, Table II.). Generally speaking, previous currents in either direction cause  $\Delta$  to increase, but after the current has been on for some time in the  $\beta$  direction, a reversal for a short period seems to assist the formation of the film. Experiment 6, Table I., shows very markedly the effect of unclean electrodes. It is noteworthy that, when the currentdensity in the  $\beta$  direction is at first of a value  $\Delta'$  greater than  $\Delta$ , the rapidity and completeness of the film-formation depends upon  $\Delta' - \Delta$ .

Table I.—Showing Effect of (1) Size of Anodes, (2) Previous history of Electrodes.

k = constant of galvanometer = 000365 ampere.

S=surface of anode= $l \times 06$  sq. cm. approximately.

l = length of anode.

The electrodes used were of platinum, one of them being a plate 40 millim.  $\times$  8.5 millim., the other a wire ·2 millim. diameter, whose length was varied during the experiment. These were placed in strong pure  $H_2SO_4$ , and a battery with an E.M.F. of 6 volts employed.

Remarks.	l.	C	Δ.
	****		ampere
1 Had been passing support a long time	mm.	o minoro	per sq. cm.
1. Had been passing current a long time in $\beta$ direction	20	ampere. $k 287 = 105$	-87
2. Ditto	10	$k \ 140 = 0511$	.85
3. Washed and heated electrodes	,,	$k \ 100 = \cdot 0365$	·61
4. Current on in a direction for 15	,,	100-0000	01
	11	k 90=.0328	•55
seconds	"	k 92=·0335	•56
6. Wiped electrodes with paper. Shows	"		
influence of unclean electrodes	,,	$k\ 240 = \cdot 0876$	1.46
7. Washed and heated electrodes	,,	$k\ 110 = 0402$	·67
8. Current on in a direction for 30			
seconds	,,	$k \ 150 = 0547$	.91
9. Ditto for 45 seconds	99	$k \ 120 = 0438$	· <b>7</b> 3
10. Broke circuit; lifted electrodes up			
and down in the liquid several times.			
Film evidently not thoroughly re-			
moved by this process, and there-		7 50 0055	
fore easily reformed	"	k 70 = .0255	•43
11. Broke circuit; lifted electrodes out			
of liquid for 10 seconds, then moved			
them up and down in liquid for		k 130=·0475	.79
30 seconds	5	k = 63 = .0230	.77
13. Current on in a direction for a moment	-	k = 67 = .0245	-82
10. Current on in a unfection for a moment	27	n 01 = 0210	02

The resistance of the voltameter was, as estimated by Ohm's method, 45 ohms in the  $\alpha$  direction of the current, and 4500 ohms in the  $\beta$  direction when the film was formed. Increasing the E.M.F. of the battery made no difference in the value of C.

Table II.—Showing Effect of (1) Change of Currentstrength, (2) Previous history of Electrodes.

k = constant of galvanometer = 00051 ampere.

The electrodes were of platinum, size not noted, and the electrolyte was strong pure  $H_2SO_4$ .

Treatment of Electrodes.	Ohms in circuit with voltameter.	Deflection.	${f R}{f e}{f m}{f a}{f r}{f k}{f s}.$
1. (During experiments 2. 1-7 the current	30 20	117 162	Deflection steady.
3. was kept continu-	15	191-194	,, less steady. Vibrations more marked.
4. ously on in the		235–238	Viorations more marked.
5. film-forming $(\beta)$ direction.)		315-321	Vibrations, which were not regular.
6.	3	365-370	
7.	ő	4	Film formed; the deflection being reduced immediately to 4.
8. Short-circuited vol-		4	
9. Current reversed for		4	2) 2) 2)
an instant 10. Electrodes heated to	3	4	" "
redness	3	4	› <b>› ››</b> ››
tameter for a time.	6	4	,, ,, ,,
12. ,, ,,	10	212	" " "
13. Current reversed for			
an instant	9	230-234	
14. ,, ,,	7	235-250	
15. ,, ,,	6	250-20	Film formed; deflection reduced to 20.
16. ,, ,,	5.5	270-20	Deflection at first 270, then fell gradually to 150, and then a rapid fall to 20.
17. Electrodes reheated.	5.5	220–20	Deflection fell gradually to 20.
18. Current reversed an instant and then voltameter short-circuited		270-300	20.
19. ,, ,,	5.5	275-310	
20	5.5	280-300	
21. Electrodes reheated 22. Current reversed an instant and then		200-4	
voltameter short- circuited	5.5	270-310	
stand 5 minutes in the acid	5.5	4	Film quickly formed.

The method of placing the anode in the acid has an important influence upon the value of  $\Delta$ , as the following

experiments show:-

Exp. I.—The end of a Pt wire used as an anode was immersed in the acid, and then the film was formed by the lowest value of the current-density. The anode was then gradually lowered into the acid, when it was noticed that the film was formed over the whole wire. When the wire was lowered rapidly the film remained on the lower part for a time, but the upper portion was conducting, as evidenced by the escape of gas from it.

Exp. II.—The reverse of the previous experiment is not easy to perform. If we have at first the whole length of the wire immersed and use a current-density just less than  $\Delta$ , and then try to form the film by diminishing the length of the wire immersed—the strength of the current meanwhile

being kept constant—it is difficult to do so.

d. Persistence of Film.—The disappearance of the film was generally tested for by means of a weak current as follows:—Knowing what deflection would be obtained, when the film was not formed, with a certain large resistance in circuit, then after the film had been formed the resistance was increased to this value: if the current corresponding to this resistance without the film was able to pass, it showed that the film had been totally removed, and generally, from the amount of current which did pass, could be estimated the degree of disappearance of the film.

After the formation of the film there are no signs of its disappearance as long as the battery is left in circuit with the voltameter, but if the circuit be broken the film tends to disappear, the rate of disappearance depending on the completeness with which the film had previously been formed. It disappears very quickly if the voltameter be short-circuited,

and instantaneously if the current be reversed.

The film is removed at once if the anode be taken out of the liquid and wiped, but if the anode be left in the liquid—the electrodes being still in connexion with the battery—the anode may be moved about in the liquid or rubbed with a glass rod without destroying the film. If the rubbing be vigorous the film will be partially destroyed, but on ceasing the friction the film immediately reforms. The anode may be removed from the liquid and held in the air some time without thoroughly destroying the film. When in the liquid a stream of air-bubbles may be blown violently against the anode without destroying the film, but if the anode is removed from the liquid a moderate current of air blown against it removes the film.

Vibrating the anode, when the film is on the point of being formed, certainly helps its formation, but after the film has formed violent agitation does not affect it, though by this means the outer layers, at least, of the sheath of bubbles round the anode may be removed. We have tried the effect of mounting the voltameter on a whirling table, the electrodes being kept fixed, and find that we can form the film when the voltameter is rapidly rotating. The value of  $\Delta$  with the rotating voltameter was little, if any, different from that obtained when it was stationary. Touching the anode with an iron wire immediately destroys the film; this is also the case if a platinum wire is used to touch the anode, but when the platinum wire is not too large the film reforms.

According to our measurements the E.M.F. of polarization is about 2.5 volts; if after the film has been formed we reduce the battery E.M.F. to a value rather less than this without breaking circuit, we find that the film disappears more slowly

than if the circuit is broken.

e. Influence of Degree of Concentration of Acid.—A small percentage of water appears to exercise but little influence on  $\Delta$ , but when the liquid contains as much as 70 per cent. water by volume we have been unable to produce the film. The general effect of dilution is exhibited in the following tables; the variations of  $\Delta$  for percentages of acid between 98 and 87 being probably due to accidental causes. The dilution seems also to diminish the rate at which the film is formed.

TABLE III. - Showing Effect of Concentration.

A. Impure H <sub>2</sub> SO <sub>4</sub> . Temperature 9°·2 C.		B. Pure $H_2SO_4$ .			
Percentage of acid by vol.	Relative values of $\Delta$ .	Percentage of acid by vol.	Temperature.	Relative values of $\Delta$ .	
98 97 96 95 93 90 87 82 78	248 273 272 272 242 250 250 340 360	70 60 50 40* 30	+11° C. +13°-5 C. +14°-3 C. +15°-8 C. -10° C.	25 62 150 500 <b>N</b> o film.	

<sup>\*</sup> The production of the film in acid of this degree of dilution effectually disposes of any idea that hydroxyl can have any influence in forming the film. See footnote of our former paper (Phil. Mag. April 1888, p. 279).

f. Influence of Temperature.—Inspection of the curves (figs. 6, 7, and 8), giving the variation of the film-forming current-density with the temperature will show that  $\Delta$  is markedly affected by a change of temperature, and particularly so at the higher temperatures; an increase in the temperature requiring a corresponding increase in  $\Delta$ , the rate of increase of  $\Delta$  with temperature being greater at the higher temperatures. The observations from which the curves are drawn were obtained in the following manner:-The anode and kathode were placed in separate beakers, each containing strong pure H<sub>2</sub>SO<sub>4</sub>. Connexion was made between the two vessels by means of several inverted U-tubes filled with acid. The beaker containing the kathode was kept at a constant temperature throughout. Starting with both beakers at about 15°C. the current was put on in the B direction, and the current-resistance varied until the film was formed and the corresponding value of  $\Delta$  noted. The current was then reversed for a moment in order to remove the film, the beaker containing the anode heated, and for every few degrees of rise of temperature  $\Delta$  was found as just described. In the case of falling temperatures the process was somewhat different and yielded more regular results. After  $\Delta$  had been found for the highest temperature, the resistance in circuit was slightly increased, the film being removed by reversing for an instant, and the anode vessel allowed to cool. The temperature was then noted at which the film again formed with the slightly diminished current. This procedure was repeated until the anode vessel had cooled down to the desired extent.

g. Influence of Viscosity.—It was thought probable that if we made dilute  $H_2SO_4$  (say 10 per cent. acid) sufficiently viscous that the film would be produced; but negative results have accompanied the addition of both glycerine and gelatine to the dilute acid. With a 50 per cent. acid to which 2 per cent. of gelatine had been added, the value of  $\Delta$  was reduced to one third by this addition. Addition of glue to strong  $H_0SO_4$  has a similar effect in lessening the value of  $\Delta$ \*.

h. Effect of Platinizing the Electrodes.—Some difficulty has been experienced in trying to estimate the effect which platinizing a platinum electrode has on the value of  $\Delta$ , on account of the impossibility of accurately measuring the surface of the platinized wire. There is no doubt that after platinizing a few moments much greater currents than that

<sup>\*</sup> It is perhaps worth mentioning that a jelly made of glue and water gave the film at the kathode. In one case, when the electrodes were a wire and a Wollaston's point, the resistance was 2000 ohms when the wire was kathode, and 45,000 ohms with the point as kathode.

which produced the film before platinization are now unable to do so, but whether the surface of the anode has increased by platinizing in the same ratio we are unable to say. In one case, in which before platinizing the film was formed with a current of 70 divisions, after a few moments' platinizing the film would not form with currents as high as 300 divisions.

#### 3a. Experiments with H<sub>2</sub>SO<sub>4</sub> and Carbon Electrodes

In these experiments we at first found considerable difficulty owing to the disintegration, during electrolysis, of the various kinds of carbon. Carré-prepared carbons, gas-carbons, and graphite (from lead-pencils) all behaved in the same way. On making circuit no gas at first comes from the anode, but eventually the outer shell breaks off and gas is evolved \*. It occurred to us that the coherent carbon filaments used in incandescent lamps might be free from this objection, and this conjecture was found to be justified. At first filaments from Swan lamps were used, and afterwards some kindly supplied by Messrs. Woodhouse and Rawson. With either of these carbons we were able to electrolyze strong H<sub>2</sub>SO<sub>4</sub> without any disintegration or coloration of the liquid.

Using these carbon filaments we were able to readily produce a film at the anode which had the same general properties as that obtained with platinum. To make sure that the film was not due to any coating of oxidizable material the filaments were boiled in aqua-regia and well washed, but this had no influence in preventing the formation of the film. Platinized carbon behaves as regards the film-formation exactly like platinized platinum. The insulating condition, with carbon filaments, is accompanied, as in the case of platinum, by the formation of a gaseous sheath round the anode.

#### 3 b. Experiments with H<sub>2</sub>SO<sub>4</sub> and Gold Electrodes.

Some fine gold wire, sold to us as pure by Messrs. Johnson, Matthey, & Co., and a piece of platinum foil were used together as electrodes in strong pure H<sub>2</sub>SO<sub>4</sub>; the platinum and gold being placed in separate limbs of a U-tube. The behaviour of this combination was very peculiar. film readily formed when the gold was anode, but no sooner

<sup>\*</sup> This behaviour of carbon has been noticed by Gore and others, and more recently studied by Debray and Pechard (Compt. Rend. cv. pp. 27-30). These observers, using gas and other kinds of carbon purified by Cl at high temperatures, found that the gas evolved at the anode during the electrolysis of H<sub>2</sub>SO<sub>4</sub> was a mixture of CO<sub>2</sub> and O. The black powder formed on disintegration (after being washed and dried) deflagrated at a temperature below red-heat, evolving CO and CO.

had it formed than it began to disappear again, and did not reform until the circuit had been broken. On making the gold wire the anode, after the current had been in the previous direction, it was noticed that one of two things happened, either (1) the deflection at first was large, and decreased rather quickly to a small value, then increased gradually to its former value, or (2) the deflection at first was small and then made a sudden jump to a high value, at which it remained. The gold wire used was very rapidly eaten away.

## 4. Experiments with other Electrolytes and Platinum Electrodes.

a. Phosphoric Acid.—Efforts to produce a definite film have been unavailing. We have tried various solutions (including some quite viscous), and although we have found that there is a difference of deflection in the two directions of the current, the electrodes being a point and a plate, we are disposed to attribute this mainly to polarization. At the same time there certainly is evidence of a difference of transition resistance in the two directions, for in one case, using a battery E.M.F. of about 18 volts, the deflection when the point was anode was double that with the current reversed. This indicates that in the latter direction there is a higher transition resistance, for any difference of polarization in the two directions would probably be small relative to

the E.M.F. employed.

b. Caustic Potash.—Different strengths of solution up to saturation, and a battery E.M.F. up to ten volts were used, but no definite film could be obtained. On adding glycerine to the solution, in order to increase its viscosity, the transition resistance, as measured by Ohm's method, was greater with the point anode than when kathode; in one experiment the resistances were 37 and 3.5 ohms respectively. Attempts were afterwards made to repeat the effects obtained by Ohm, with solutions of caustic potash, and for this purpose a battery of 3 Daniells was employed. The differences of the deflections in the two directions, and also the fall of the deflection obtained after making circuit, were generally to be attributed to polarization; but using certain currents a tendency towards the formation of a transition resistance could be traced, as evidenced by the table below, the numbers of which were obtained by Ohm's method.

Table IV.—Irreciprocity with Platinum Electrodes in KHO\*.

				Point anode.	Plate anode.
Resistance of voltameter, Exp. 1		111·3 ohms.	33.5 ohms.		
>3	,,	,,,	2	120 "	32 ,,
Polarization	,,	,,	1	2.65 volts.	2·12 volts.
,,	,,	,,	2	2.65 "	2.16 "
Current through	23	23	1	$\cdot 00265$ ampere.	·0178 ampere.
37 37	"	,,	2	.00247 ,,	0149 ,,

c. Other Liquids.—No film was obtained with platinum electrodes in the following liquids:—(1) Pure fuming HNO<sub>3</sub>; (2) a mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, the former being in excess; (3) strong HCl; (4) a mixture of HNO<sub>3</sub> and HCl in equal parts. The film was obtained with strong H<sub>2</sub>SO<sub>4</sub> in which CrO<sub>3</sub> had been dissolved, but no remarkable features were noticed.

#### 5. Experiments on Soap and Sodium Benzoate.

A piece of common white soap was cut in the form of a cylinder 4 cm. long and 1 cm. diameter. It was protected by a glass tube, and mounted so that platinum plates pressed against its two ends. The resistance, as measured by Ohm's method, showed a gradually increasing value, the battery being kept, in circuit, from 1080 to 23,000 ohms, at which it remained constant. The polarization was taken for various times of charge, but showed but little variation. Measurements of the resistance of the soap with a battery in its circuit were also made by Kohlrausch's method, the results confirming those previously obtained by Ohm's method. With solutions of soap the solid soap acids were separated out, but there were no signs of any film-formation.

In many respects a solution of sodium benzoate resembles soap, for benzoic acid is but little soluble in water, hence it was thought that an electrolytic deposit at the anode might stop the current. This was found to be the case; different

<sup>\*</sup> Further measurements are being made both with KHO and other liquids by means of the method of Fuchs, which with certain precautions now appears to us to be the one best adapted.

strengths of sodium benzoate giving the film without difficulty. Careful observation showed that with weak currents the oxygen produced at the anode was able to break through the layer of benzoic acid, and thus prevent the film-formation; but with strong currents the solid acid obtained the mastery, the oxygen then not being able to break through and so disperse the acid. Hence, with strong currents a film, consisting of solid benzoic acid in which oxygen bubbles were entangled, was formed round the anode, thus stopping the current.

## 6. Discussion of the possible Causes of the Film.

The film in H<sub>2</sub>SO<sub>4</sub> with platinum electrodes is in many respects very analogous to those obtained in the same liquid with oxidizable electrodes, and also to that which causes the passivity of iron, in which cases a solid oxide or sulphate layer on the anode is acknowledged to be the cause of the The non-formation of the film with platinum electrodes in H<sub>2</sub>SO<sub>4</sub> below a certain strength, the increase of  $\Delta$  with the temperature, the fact that the film disappears gradually on breaking the circuit, and immediately on reversing the current, all point, it may be argued, to a solid oxide or sulphate layer on the platinum anode; the solubility of this layer varying with the concentration and temperature of the acid, and its disappearance being immediately caused by a deposit of nascent H on it. although platinum is usually regarded as non-oxidizable, yet under the condition of electrolysis, which is attended by the production of ozone in quantity at the anode, it seems quite possible for an oxide of platinum to be formed. This view was strongly upheld by De La Rive. In his 'Electricity,' vol. ii. p. 410, he says that "the part played by platinum is very remarkable, for although it passes for being not oxidizable, yet it comports itself like the metals that are so, but in a feeble degree." The blackening of platinum electrodes in dilute H<sub>2</sub>SO<sub>4</sub> caused by the passage of alternate or direct intermittent currents (the former being more effective) is urged as a proof that platinum is attackable by the electrolytic gases. De La Rive insists upon the view that the blackening is due to a series of oxidations and reductions of the platinum, the oxidation with the direct currents being due to the O dissolved in the acid. Another view, mentioned by Wiedemann, is that the alteration of the surface is caused by the mechanical action of the hydrogen, which is first occluded and then evolved again from the electrode when the current is diminished or reversed. De La Rive gives other evidence in support of his theory of the successive oxidation

and reduction of platinum, and explains the catalytic action of platinum according to this view. Schönbein, on the other hand, quite as firmly upheld the theory that the oxygen did not combine with the platinum, but formed a condensed gaseous film on its surface. Faraday also seems to have shared this view\*.

Again, it should be mentioned that, using large currentdensities, McLeod † found that very fine platinum wires were destroyed during the electrolysis of H2SO4 of density 1.3; but whether this was due to actual solution of the platinum or to its disaggregation or to traces of Cl is doubtful. If solution of the platinum really occurs, it would support the theory that the film is due to a solid oxide or sulphate layer. as in the case of the oxidizable electrodes. In this relation an experiment of ours may be quoted. A platinum wire was carefully cleaned and weighed, and then used as anode in strong H<sub>2</sub>SO<sub>4</sub>, the film being then formed on it. It was taken out quickly, and wiped (with asbestos), which, as said previously, removes the film. The anode was then replaced, the film again formed and again wiped off. This was repeated a great number of times, but no variation of the weight of the anode could be detected after the experiment, nor was there any difference in the appearance of the wire. We have further electrolyzed sulphuric acid with platinum electrodes continuously for many hours without finding any variation in the weight of the electrodes. Negative experiments of this nature, however, cannot be regarded as having much

In endeavouring to ascertain the nature of the film we are met by the difficulty that removal from the acid speedily brings about the destruction of the film, and other evidences of its instability have been previously given. Thus, there is no possibility of applying the direct tests that have led to the generally accepted view in the case of the oxidizable electrodes, and although the film sticks with some firmness when in the electrolyte and the battery-current is not broken, yet there are no chemical tests which can be directly applied under these conditions that can be thought very satisfactory. We may, however, mention that the film remains undisturbed when a stream of hydrogen is passed in small bubbles over the anode, but is speedily removed if the acid round the anode be diluted by a stream of water. The formation of the film with

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<sup>\*</sup> Exp. Res. vol. i. p. 165. It may be noted that Dulong and Thenard have shown in a research (*Ann. de Chim.* vol. xxiii. p. 440, 1823, and vol. xxiv. p. 380, 1823) that all bodies have the catalytic power, more or less. † Journ. Chem. Soc. vol. xlix. p. 591.

carbon electrodes, the non-formation of the film with platinum electrodes in various oxidizing agents, and other minor properties, which will be found in the previous part of the paper, have led us to doubt the accuracy of the oxide theory in the case of platinum or carbon electrodes, and to provisionally adopt another theory, as indicated below.

The behaviour observed at the anode in the case of the electrolysis of sodium benzoate solution suggests that the badly-conducting sulphuric acid which appears, in electrolyzing that liquid, at the anode, may under certain conditions be able to stop the current. In discussing such a hypothesis

we have to remember:—

(1) That the specific resistance of H<sub>2</sub>SO<sub>4</sub> increases very

rapidly with the degree of concentration.

(2) That the concentration of the acid at the anode during electrolysis is partially prevented (a) by the evolution of oxygen (as we have pointed out in Phil. Mag. April 1888, p. 283), and also (b) by its dilution, the rapidity of which depends on the viscosity and strength of the acid solution used.

(3) That a certain amount of oxygen forms a gaseous layer

on the anode.

Bearing these points in mind, we will examine whether they are sufficient to explain our experiments.

Firstly. With low current-densities the concentrated acid will be formed in quantity too small to withstand the two

causes tending to cause its dispersion.

Secondly. With greater current-densities the rate of formation of the concentrated acid will overcome the rapidity of its dilution, and the resistance of the layer of acid round the anode may increase so rapidly as to form an insulating film, before enough gas has been evolved to cause its destruction; the gas which has been produced becoming entangled in the viscous concentrated layer, which, once formed, will not be

easily removed by friction, &c.

Third/y. With still higher current-densities, though there will be a greater tendency towards the formation of this layer immediately the circuit is made, yet it is conceivable that more gas will be produced in the same time than can be prevented from escaping, and thus destroying the non-conducting layer; for it would be expected that the tendency of the gas to escape would increase at a greater rate than the tendency of the acid layer to prevent the escape. An upper limit to the current-density ought therefore to be discoverable beyond which no film can be produced. In the case of foil electrodes placed horizontally with only the lower surface exposed

to the acid, we have succeeded in obtaining such an upper limit. The discovery of an upper limit makes some of our experiments of less value, for where we have stated that no film has been obtained, the non-success may be due to failure in fixing on the right limits of current-density. It also explains the peculiar jumps in the current which we have at times observed in using platinum electrodes in strong  $H_2SO_4$ . These jumps, which were of a similar kind to those which we obtained with gold electrodes, are probably due to the current-density used being near the upper limit when small causes, such as the heating of the liquid, would involve the disappearance of the film\*.

This provisional hypothesis likewise accounts for the nonformation of the film in dilute  $H_2SO_4^{\dagger}$ . Here the rate of dilution (even if the electrolyte be made viscous by the addition of glycerine) of the concentrating layer will be more rapid, and hence a greater length of time would be required to produce a thoroughly concentrated layer. But the longer the time that elapses before this is attained, so much the greater must be the quantity of oxygen produced. Thus, just as in the case of current-densities above the upper limit in strong  $H_2SO_4$ , the formation of film will be prevented.

The less rapid increase of the specific resistance with the degree of concentration in the cases of H<sub>3</sub>PO<sub>4</sub> and KHO probably explains the difficulty found in obtaining such a high degree of insulation as we have observed with H<sub>2</sub>SO<sub>4</sub>.

Some other aspects of transition resistance, evidenced by some experiments not included here, will be considered in a subsequent paper.

### XVII. On a Practical Constant-Volume Air-Thermometer. By J. T. Bottomley, M.A., F.R.S.‡

In the fourth Mémoire of his celebrated Relation des Expériences, published in 1847, Regnault gives cogent reasons for preferring the air-thermometer before any other as the instrument by means of which temperature may be

<sup>\*</sup> We are not disposed to think that the jumps obtained with gold are due to the same cause. Gold really comes under the head of attackable electrodes, and the phenomena with it are, therefore, probably of a more complicated character than with either platinum or carbon. Palladium, in this respect, must be classed with gold, for when used as anode in moderately strong sulphuric acid, it dissolves.

<sup>†</sup> The results obtained by Christiani, we believe, may also be explained by this hypothesis.

<sup>†</sup> Communicated by the Author, being a paper read before the Royal Society of Edinburgh, Jan. 6, 1888, with an addition of June 5, 1888.

defined, and high temperatures determined. The thermodynamic researches of Sir William Thomson have furnished an absolute thermodynamic definition of temperatures; and the experimental researches of Dr. Joule and Sir William Thomson have established the practical agreement of Regnault's air-thermometer with the thermodynamic scale of temperatures. Lastly, the air-thermometer is the only instrument known at present, with the exception of a mercurial thermometer which has been compared with an air-thermometer, by means of which temperatures higher than, say, 150° C. or 200° C. can be determined within 3° C. or 4° C.\*

In experimenting on the resistance of platinum and carbon filaments at high temperatures, in connexion with a research on thermal radiation with which I have been engaged, I have used air-thermometers of various forms; and I have recently been using a constant-volume air-thermometer, which I first described to Professor Gray, of University College, Bangor, just two years ago (January 1886), and partially constructed for him at that time. It is this instrument, greatly improved as to practical details, which I now desire to bring before the

Royal Society.

The best known constant-volume air-thermometer is that of Jolly of Vienna. It is a convenient instrument, and is fairly accurate for moderate temperatures; but for high temperatures a correction, which it is necessary to apply on account of expulsion of air from the heated part of the thermometer, becomes serious, at any rate with the dimensions commonly given to the instrument. It has also some other defects, among which may be mentioned difficulties as to the capillary surfaces of the mercury, want of flexibility or adaptability for various positions, and the proximity of the manometric column to the heated regions.

The modifications which I have made in the construction of the air-thermometer have a threefold object, one part of which is to improve on the accuracy of the instrument, and reduce to the minimum that is practicable the correction above referred to for the air expelled by heat from the thermometer-bulb or air-reservoir. A second object is to increase the range of the instrument by giving it a form in which the hard Bohemian glass can be used in the construction of the part to be heated. The third object is to make that part of the thermometer which is to be heated, and which, in the use of the

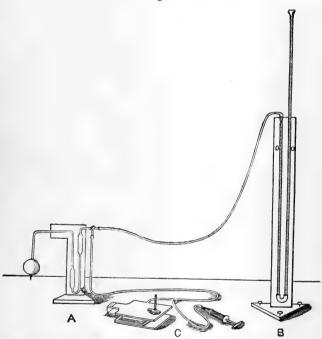
<sup>\*</sup> Mr. H. L. Callendar has proposed to use the resistance of platinum for thermometric purposes; but in this case also the final standard of reference is the air-thermometer.

instrument, must be put in position with other pieces of experimental apparatus, of such a form as to be easily handled.

For all these objects I find it most convenient to construct separately the manometric columns, and the air-reservoir with its volume-indicator; connecting these two parts of the instrument only by flexible tubing. This arrangement necessitates an apparatus for regulating the pressure under which the air in the thermometer is maintained.

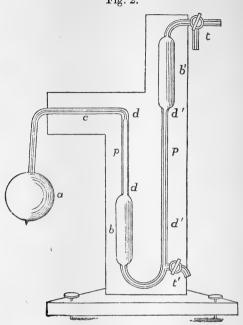
The complete instrument is shown in fig. 1. A is the airreservoir and volume-indicator, B is the manometric gauge, and C is the pressure-apparatus.

Fig. 1.



The air-reservoir and volume-indicator I shall call, for brevity, the volume-gauge. It is made in two forms (figs. 2 and 3)—the form shown in fig. 2 for the lower, and the other for the higher temperatures. The bulb, a, which is generally either globular or cylindrical, is connected by a very fine capillary tube, c, with a somewhat wider tube, d. At b, b' there are two cylindrical bulbs of the same size. The tubes dd and d'd' are of precisely the same diameter, being cut from the same length of uniform glass tubing. The diameter of this tube is about 1 millim. It is such tubing as is used for the

fall-tubes in a Sprengel pump. t and t' are two stop-cocks; t being a three-way stopcock, connecting together the Fig. 2.



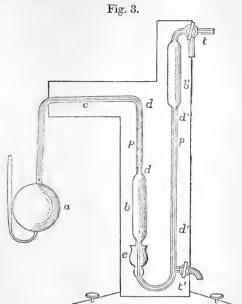
volume-gauge, the manometric gauge, and the pressure-pump; and t' is a stopcock used for adjusting the quantity of liquid

in the volume-gauge.

The object of the two cylindrical reservoirs b and b' in the volume-gauge is to give space into which the air in the bulb a may expand during heating, or in which a supply of the air may be kept during the cooling of the thermometer. The tube d is very small in capacity in comparison with the bulb; and were it not for these reservoirs, a very small change in temperature would cause the air to be driven out round the bend of the U, or the liquid in the bend to be drawn over into the bulb, unless the observer were incessantly on the watch to prevent this occurring by regulating the pressure.

The U of the volume-gauge is filled so full of liquid that the equilibrium reading is taken at the points pp of the tubes d and d; and both in the selection of the tubes c and d, and in the glass-blowing at the junction, as well as in the adjusting of the quantity of liquid in the bend, the endeavour is made to keep the volume of the air-space between the bulb and the point p as small as possible, consideration being given to the

capillarity of the tube d. Either mercury or sulphuric acid may be used in the volume-gauge. I prefer sulphuric acid on



account of its smaller density. The greatness of the density of mercury, and the uncertainty of its capillary action, make its use very liable to produce serious errors in reading. But, on the other hand, in the case of sulphuric acid, the wetting of the tubes, which constitutes its advantageous quality so far as capillarity is concerned and gives regularity of capillary action which mercury never possesses, renders watchfulness necessary to keep the acid well clear of the fine tube c. If once the acid is allowed to enter that tube, it tends to form beads and to make its way along it towards the bulb.

The manometric tube is simply a U-tube capable of giving a difference of levels of from 100 to 150 centimetres of mercury, and wide enough to make capillarity very small and difference of capillarities in the two tubes negligible. With a tube giving a difference of levels of 150 centimetres, a temperature of about 550° C. may be reached, starting with air at normal density at common temperatures. The difference of levels may be read by means of a kathetometer, or, what is preferable, the tubes themselves may be graduated to millimetres. The tubes which I use are graduated from a zero

line which is at the middle of the long branch of the U (see fig. 1). The longer tube is numbered upward and downward, and the shorter downwards, from the zero line, and the mercury is filled in so as to stand at the zero in both branches when there is no difference of pressure, and thus the sum of the readings of the two tubes is equal to the difference of pressures when any difference of pressure exists.

The pressure apparatus consists of a simple pressure-syringe which forces air into a small air-bag of india-rubber fortified with canvas. The air-bag is placed between two boards, which are connected by a leather hinge and pressed together by means of a nut which works on a wooden screw. The air-bag is also connected by means of a T-tube with the three-way stop-cock t'; and, by means of this stop-cock, the air presses both on the liquid in the volume-gauge, and on the shorter column of the manometer. The india-rubber tubes used for these connexions require to be strengthened with canvas to resist the pressure.

The form of volume-gauge shown in fig. 3 is designed for use at very high temperatures. It is made in two parts, which are connected together at the cup e (shown enlarged,

fig. 4). The bulb and tubes c, d, and bare made of hard Bohemian glass; the remaining part of the gauge is of German glass or English flint glass. The stopper of the cup e is made to fit the throat of the cup closely, and just below the throat an enlargement f is blown out, through which the elongated part of the stopper passes. The stopper is fastened air-tight into the cup with German "Siegelwachs;" and the object of the enlargement is to furnish a cushion of air which prevents the liquid of the volume-gauge from coming in contact with the cement. making of this joint is a little troublesome, and it requires to be protected against radiation from the hot source. There are various stoppers and joints well known, which prevent leakage inwards from without; but it is much more difficult to find an efficacious stopper which will act against pressure from within outwards.

The thermometer-bulb is filled with perfectly pure dry air, and it is desirable to have the bulb filled with such a quantity of air that the pressure is approximately that of a normal atmosphere when the temperature is freezing. For, if the quantity of air be considerably greater than corresponds with this condition, there is a loss of range in the instrument; whereas, if there be but a small quantity of air, there is a tendency for the liquid of the volume-gauge to be drawn over into the bulb when the temperature of the room comes down (as in winter it may) to about the freezingpoint, unless the instrument be left with the three-way stopcock closed and the air under diminished pressure. special circumstances the quantity of air may be made to suit the conditions; for, as Regnault has shown, the results obtained with the instrument are but very slightly affected by the initial pressure of the air, and this with very wide limits; and by commencing at common temperatures with air of small density, very low pressure, the upper limit of the range may be extended without increasing the length of the manometric tubes.

The filling I accomplish in the following way:—The proper quantity of liquid is first introduced into the volume-gauge, and the stop-cock t helps in introducing the liquid and in adjusting the quantity. For this and the subsequent operations I use a good Bunsen water-aspirator, with a Woulfe's two-necked bottle interposed between the aspirator and the work, and a good length of small-bore non-collapsible indiarubber tubing. With the india-rubber tubing the apparatus to be exhausted can be turned into any required position while the exhaustion is being carried on, and air-bubbles can be got rid of with ease.

When the volume-gauge has been supplied with liquid, I connect the three-way stop-cock t' to the aspirator, and draw the whole of the liquid up into the bulb b' and the tube leading up to the stop-cock itself. The size of the bulbs and of the tubes is, as has been explained, such that when this has been done the bulb b is empty as well as the tubes on the left-hand side of the gauge almost down to the bend. The three-way stop-cock is then closed, and the aspirator disconnected.

I now, with the help of a temporary three-way stop-cock, connect together the tail-piece of the bulb shown in fig. 3, the aspirator, and a train of drying and purifying tubes (sulphuric acid and caustic potash). The arrangement is such that, on turning the tap of the three-way stop-cock into position No. 1, the aspirator draws the air out of the bulb; while, on turning it into position No. 2, air flows into the bulb passing through the drying tubes. The bulb is emptied and refilled many times; and during the process the bulb and

all the tubes are heated with a Bunsen flame very nearly to the melting-point of the glass\*. When it is perfectly certain that there is nothing but pure dry air in the bulb and tubes, these are allowed to cool with free passage to the atmosphere through the drying-tubes. The bulb is then surrounded with broken ice, and the three-way stop-cock t' is opened. The liquid of the volume-gauge now finds its level; and, noting the barometer roughly (merely to know approximately the pressure), I seal the tail-piece at the extremity. The bulb now contains about the quantity of air required, and it is only necessary to remove the tail-piece. For this purpose the ice is taken away, and the liquid of the gauge is once more drawn back to a considerable extent, thus making a partial vacuum to avoid blowing out of the air during sealing. The blowpipe-flame can then be applied, and the sealing finished off as in fig. 2. Finally, the manometer and pressureapparatus are connected to the volume-gauge, and the constant of the instrument is obtained by determining the pressures required, including the barometric pressure, to bring the liquid of the volume-gauge into the marked position. first at the temperature of melting ice, and then at the temperature of steam at normal pressure. When reading the standard barometer, I also, in accordance with a most convenient suggestion by Professor Quincke, read at the same time my standard aneroid; and this for most purposes, with occasional comparison with the standard mercurial barometer, is amply sufficient to give the barometric variations. As in the case of the mercurial thermometer, so also in the airthermometer there is sure to be a secular contraction of the bulb; and, with the large bulbs used for the air-thermometer, it is quite possible that the redetermination of the constant of the air-thermometer from time to time may be necessary.

Convenient formulæ for calculating temperatures from the indications of the air-thermometer are easily obtained. Such formulæ were given by Jolly (Jubelband von Poggendorff's Annalen), who also made fresh determinations of the expansion of air and other gases. Some of these formulæ are quoted in the Leitfaden der Praktischen Physik of Kohlrausch; but

<sup>\*</sup> By this process every trace of moisture and condensed air is driven up from the walls of the tube; and, the bulb being filled with perfectly dry air, it seems certain, from the experiments of Bunsen and from some which I have myself carried out, that there is no subsequent perceptible condensation of air at the surface of the glass, such as has sometimes been supposed to vitiate the readings of the air-thermometer. Air only condenses on the surface of the glass when there is moisture present—at any rate in such quantity as would be perceptible in a case like the present.

curiously enough there is nothing said in the description of the air-thermometer by Kohlrausch as to determination of the boiling-point, the "ice point" merely being determined. An experimental determination of each point is, however, absolutely essential.

#### Addition, June 5, 1888.

Shortly after the reading of the foregoing paper, I commenced to use the coal-gas oxygen blowpipe-employing Fletcher's oxygen blowpipe and oxygen supplied in steel cylinders by the Scotch and Irish Oxygen Company (Brin For convenience these cylinders, with the automatic apparatus supplied by the company for reducing the pressure of the gas, leave nothing to be desired; and the use of the oxygen blowpipe makes easy and simple many operations which were formerly all but impossible. In particular, the working of Bohemian tubing becomes, without the slightest exaggeration, as easy as that of common flint or soft German glass; and in addition it is a perfectly simple matter to make a junction between flint glass and Bohemian glass tubing (Bohemian glass does not join well with soft German tubing). Another great advantage in the use of oxygen with the Bohemian glass is, that the glass does not become porcelainised when worked with this flame, as it does when worked with the ordinary flame.

With this new power to assist I have now abandoned completely the form of gauge shown in fig. 3, and instead I am using a gauge in which the main part is made of flint glass (stop-cocks of Bohemian glass cannot, so far as I know, be procured), but in which the air-bulb a and capillary tube c are made of Bohemian glass, and the two glasses joined together a little below the bend at the top of the tube dd. I have not yet been able to obtain from any of the first-class makers of Bohemian tube a supply of fine capillary tubes, but these I make for myself by fusing up a piece of thick wide Bohemian tubing and drawing it down.

# XVIII. Note on Continuous-current Transformers. By Professor Silvanus P. Thompson\*.

IT has often been proposed to distribute electric energy from central stations to local distributing stations by means of transformers, which receive small currents at high potential and transform them into large currents at low

<sup>\*</sup> Communicated by the Physical Society: read June 23, 1888.

potential. When alternating currents are employed, inductioncoils of appropriate construction are used as transformers.
But the use of such currents is attended by two disadvantages:
namely, that alternate currents cannot be used for electrochemical purposes, and that, pending the invention of a satisfactory alternate-current motor, they cannot be used for the
actuating motive machinery. When continuous currents are
used, the appropriate transformer may be one of two types
—(1) the motor-generator, (2) the commuting-transformer.

The motor-generator in its primitive form consists of a motor to receive the incoming current, geared mechanically to a generator which produces the outgoing current. A more specialized form consists of a single machine with one field-magnet and two armatures; one to receive the primary current, the other to generate the out-going or secondary current. If the two sets of armature-windings are coiled around the same core, each set of windings being furnished with an appropriate commutator and collecting-brushes, the development has reached its extreme case, the only remaining point being the proper method of excitation of the field-

magnet.

The commuting-transformer is a more complex apparatus. and has been much misunderstood. It does not necessarily involve any greater amount of sparking than any ordinary dynamo. The general principle of this species of transformer may be explained by reference to a particular type. Suppose that an armature double-wound with a primary coil to receive the incoming current, and a secondary coil to generate the outgoing current, have been provided as in the previous case, each coil having its appropriate commutator. To enable this piece of apparatus to transform the currents, it must either be allowed to rotate in a magnetic field between the poles of a field-magnet, or else the field-magnet (and collecting-brushes) must be arranged to rotate, in the opposite sense, around it. But there is a third possible arrangement, namely to rotate around it the magnetic polarity while itself remains fixed. This may be done either by rotating the brushes which bring in the primary current, the magnetic circuit being completed by a mass of iron external to the ring, or by rotating also the polarity of a fixed field-magnet constructed specially for this purpose. An external fixed ring of Cramme or Pacinotti pattern, provided with a commutator, will answer for this purpose, the current being supplied by a pair of brushes which is rotated. In such a machine obviously all the parts are stationary save the revolving brushes, which must be driven by some mechanical device. Various modifications of this idea have from time to time been suggested.

The theory of alternate current-transformers has been investigated by various authorities. It was first shown by Maxwell that where there is mutual induction between two circuits, the effect upon the secondary circuit of the presence of the primary circuit is threefold:—(a) to transform in a certain ratio the electromotive force; (b) to add to the resistance of the secondary circuit an apparent resistance equal to that of the primary multiplied by the square of the same ratio; (c) to deduct from the coefficient of self-induction of the secondary circuit a quantity equal to the coefficient of self-induction of the primary circuit multiplied by the square of the same ratio. The ratio in question was found to be the quantity

 $rac{2\pi n ext{M}}{\sqrt{4\pi^2 n^2 ext{L}_1{}^2 + ext{R}_1{}^2}}$  ;

where M is the coefficient of mutual induction, n the number of alternations per second,  $L_1$  and  $R_1$  the coefficient of self-induction and the resistance respectively of the primary circuit. In a communication made last year to this Society I showed how, assuming the proper conditions of good construction to have been observed, this ratio was equal to the ratio of the number of secondary windings to the number of primary windings in the transformer; which ratio is known as the "coefficient of transformation."

The object of the present paper is to show that in continuous current-transformers effects of the same kind exist. The investigation is of an elementary character, secondary reac-

tions being assumed to be negligibly small.

Consider a motor-generator, with double-wound armature of ring or drum type, arranged to rotate between the poles of a common fixed field-magnet. The magnetism of the latter may be considered for present purpose constant: the effect of variation in the magnetization will be afterwards considered. Let the number of armature-conductors of the primary or motor part, as counted all round the periphery, be called  $C_1$ , and that of the secondary part be called  $C_2$ . The ratio of  $C_2$  to  $C_1$  we may call the coefficient of transformation, and we shall use k as the symbol of this ratio.

Now let  $i_1$ ,  $r_1$ , and  $E_1$  stand respectively for the current, the resistance, and the induced electromotive force in the coils of the primary armature, and  $i_2$ ,  $r_2$ ,  $E_2$  for the corresponding quantities for the coils of the secondary armature. Write N for the whole number of magnetic lines passing through the armature-core. Also write  $e_1$  and  $e_2$  for the respective differences of potential at the terminals of the

primary and secondary parts.

We shall then have

 $E_1 = nC_1N \cdot 10^{-8},$  $E_2 = nC_2N \cdot 10^{-8};$ 

whence

$$E_2/E_1 = C_2/C_1 = k$$
,

whatever the values of speed and field may be. Further,

$$\begin{split} \mathbf{E}_1 &= e_1 - r_1 i_1, \\ \mathbf{E}_2 &= e_2 + r_2 i_2 \ ; \end{split}$$

whence

$$e_2 = ke_1 - r_2i_2 - kr_1i_1$$
.

Now assume that the work wasted in the armature in mechanical and magnetic friction, and in producing eddy-currents, is negligibly small compared with the work done in driving the generator part. This is, in fact, merely assuming that the machine is properly designed and constructed; for in such machines, there being no driving-belt, the only forces except gravity are centrally balanced, and mechanical friction at the bearings is a minimum; and further, if the iron core is of proper quality and quantity, and properly laminated and insulated, the losses due to hysteresis and eddy-currents are very small\*. We shall then have the work  $\mathbf{E}_1i_1$  done by the primary current (in unit time) equal to the work  $\mathbf{E}_2i_2$  done on the secondary current. Consequently  $i_1=ki_2$ . Inserting this value, we at once get

$$e_2 = ke_1 - (r_2 + k^2r_1)i_2$$
.

This shows that everything goes on in the secondary circuit as though the induced electromotive force was transformed from the difference of potentials at the terminals of the primary circuit in proportion to the respective numbers of windings on the armature, and as though there were then added to the real internal resistance of the secondary circuit a resistance equal to that of the primary winding multiplied by the square of the coefficient of transformation. If there are equal weights of copper in the primary and secondary windings, the actual resistances of the two windings will be proportional to the squares of the numbers of turns: hence the effect of multiplying  $r_1$  by  $k^2$  is to make it equal to  $r_2$ ; in other words, the added virtual resistance is equal to the real internal resistance.

$$e_2 = ke_1 - i_2(r_2 + k^2r_1 + F/i_2^2).$$

<sup>\*</sup> If F be the waste work done against mechanical and magnetic friction, the formula becomes

With respect to self-induction and its effects in such machines, it may be remembered that, in an ordinary singlewound dynamo, the effect of self-induction is to add to the armature a spurious resistance, owing to the successive stoppage and restarting twice in every revolution of the current in each section. Now if matters were so arranged in the double-wound machine that commutation of the current in any one section of the primary should occur exactly at the same instant as commutation of the current in that section of the secondary wire which was wound over the same part of the common core, it is clear that, as the currents in the primary and secondary circulate around the core in opposite senses, the stopping of the current in the one would tend to stop the (inverse) current in the other, and the starting again of the current in the one would tend to start the inverse current in the other. In other words, the mutual induction between the two sections would tend to counteract in both the effects of self-induction. In practice it is impossible to fully realize this neutralizing effect; but that it is very nearly realized is evidenced by the almost complete absence of sparking in such machines.

In the above argument it has been assumed that the magnetism of the field-magnet was constant in amount; but incidentally it was noticed that the expressions were independent of the magnetic field. The more powerful this is, the slower need the armature run to generate the respective electromotive forces. Assuming that the transformer is supplied at constant potential at its primary terminals, and that the internal resistance of the secondary winding is small, it will be self-regulating, giving a constant potential at its secondary terminals quite irrespective of the variations of its

speed with the load.

In yet one other respect does the action of the motorgenerator resemble the alternating transformer: when supplied at constant potential it is almost exactly self-regulating in respect of its automatic action in adjusting the amount of the inflowing primary current, in proportion to the outflowing secondary current. When the secondary circuit is entirely opened, the motor part runs just so fast that the back electromotive force E<sub>1</sub> in the primary part increases and dams back the primary current; only just so much flowing through as will suffice to drive the machine against the reactive forces of mechanical and magnetic friction.

Precisely similar relations to those traced out for motorgenerators hold good in the commuting-transformers. The reactions between the primary and secondary windings go on Phil. Mag. S. 5. Vol. 26. No. 159. Aug. 1888. line of contact.

exactly the same, whether the successive displacement in the polarity of the magnetization through the common core of the armature be accomplished by mechanically rotating it, or by electrically shifting the polarity of the surrounding field-magnet in a rotatory fashion. With equal weights of copper in the primary and secondary coils of the armature part, the effect of mutual induction will here also be approximately to double the internal resistance and to neutralize the self-induction of the secondary winding.

#### XIX. The Contact-Angle of Liquids and Solids. By W. F. Magie, Ph.D.\*

#### Introduction.

GAUSS, in his discussion of the theory of Capillarity, demonstrates that the surface of any liquid in contact with a solid will make with the solid a definite angle at the

The assumptions at the foundation of his

theory are the same as those made by Laplace—that the force between two molecules diminishes very rapidly as the distance between them increases, and that, nevertheless, the radius of molecular force is such as to include within it a large number of molecules. The expression for the contact-angle A (that is, the angle between the normal to the solid surface and the normal to the liquid surface at the line of contact, or, more strictly, at a distance from the solid equal to the radius of molecular force) is  $\cos A = \frac{2\beta^2 - \alpha^2}{\alpha^2}$ . The quantities  $\alpha^2$  and  $\beta^2$ are constants for each liquid and solid, depending respectively upon the forces between the elements of the liquid and those between the elements of the liquid and the solid. Upon the hypothesis that the laws of these forces as functions of the distance between the elements are the same, or that the ratio of the functions f(x) and F(x) representing them is independent of the value of x, these constants  $\alpha^2$  and  $\beta^2$  are proportional to the forces upon which they depend. Upon this hypothesis, then, there will be an obtuse contact-angle when the force between two liquid elements is greater than twice that between a liquid and a solid element. When the force between two liquid elements is less than twice and more than once the force between a liquid and a solid element there will be an acute contact-angle, which is not zero. Such an

<sup>\*</sup> Communicated by the Author. † Gauss, Fig. Fluid., Werke, vol. v. p. 69.

angle I call, in distinction from the infinitesimal contact-angle existing when  $\alpha^2$  is less than  $\beta^2$ , a finite acute contact-angle.

It seems not unlikely that such a relation may exist in many cases between the force-functions as will give rise to a finite acute contact-angle. Even if the force-functions are not of the same form, so that the proportionality assumed between them and the constants  $\alpha^2$  and  $\beta^2$  does not exist, they are probably of the same order of magnitude; so that, for certain relations between them, the constant  $\alpha^2$  will lie between the limits  $2\beta^2$  and  $\beta^2$ , and the contact-angle be finite and acute. While there is thus no theoretical reason against the existence of a finite acute contact-angle, yet no indubitable evidence has, in my opinion, yet been presented of the existence of such Such as has been given is based upon the use of methods so open to objection that it cannot be accepted as final. I have endeavoured, by the use of methods so modified as to, as far as possible, remove those objections, to establish the presence or absence of an acute finite contact-angle in the cases of the liquids which were examined. For many of them the investigations of Quincke and Traube have indicated the possibility of the existence of such an angle.

Prof. Quincke's conclusions were based upon the comparison of the results of his measurements of the dimensions of air-bubbles formed under a horizontal glass plate in the various liquids examined with those of the measurements of the rise of the same liquids in capillary tubes\*. His observations and methods of calculation have been criticised by Volkmann †, Worthington ‡, Stieg §, and myself ||, and it will not be necessary to discuss them here. A word may be said, however, in reference to a recent paper by Prof. Quincke ¶, in which he calls attention to his use of an empirical correction by which, in his opinion, the defects of his earlier method of calculation are removed. This correction is obtained by the measurement of bubbles 100 millim, in diameter, and is based upon the assumption that, at a point in the contour of the greatest horizontal section of such a bubble, the radius of curvature of that section is infinite in comparison with the radius of curvature of the vertical section. The value of the capillary constant  $a^2$ , computed on this assumption, is used as the basis for the correction of results obtained from the measurement

Quincke, Pogg. Ann. cxxxix. p. 1 (1870).

<sup>†</sup> Wied. Ann. xvii. p. 355 (1882). † Phil. Mag. xx. p. 65 (1885). § Trans. Berlin. Phys. Soc. Nov. 25, 1888.

Wied. Ann. xxv. p. 429 (1885). ¶ Ibid. xxvii. p. 219 (1886).

of much smaller bubbles. That this assumption is not admissible can be seen at once, from a computation of the correctionterm involving the semidiameter of the bubble in the formula for  $a^2$  which is given by Poisson, and presented later in this paper. It will be found that, for a bubble of the diameter of 100 millim., the correction to be applied to reduce the value of  $a^2$  obtained on the assumption made by Prof. Quincke, amounts for water to more than 5 per cent., for alcohol to nearly 3 per cent., and for other liquids to similar percentages of their respective values of  $a^2$ . Further, the application of such a correction, or indeed of Poisson's formula, as used by Prof. Quincke in his study of the capillary constants of mercury\*, to bubbles of which the diameters are rarely greater than 30 millim., is at least questionable to In no case does the application of Poisson's formula to the measurements given by Prof. Quincke reduce the values of  $a^2$ , which in the first approximation are too great, to an agreement with the results obtained from similar measurements of large bubbles, to which the application of Poisson's formula is, without doubt, admissible.

Dr. Traube presents, as evidence of the existence of a finite acute contact-angle and of its variability with temperature, his measurements of the heights of the meniscus in capillary tubes!. This height was always less than the radius of the tube, and diminished as the temperature rose. Similar results were obtained by MM. Haüy and Tremery \, and by Dr. Schiff. With regard to the results of MM. Hauy and Trémery, Laplace showed that a slight error in determining the point of contact of the liquid surface with the tube would account for the discrepancy observed, and he concludes that the experiment offers no proof of a finite contact-angle. The experiments of Dr. Traube are open to a serious objection. diameters of the tubes employed were so great, that not only is the first approximation, which Dr. Traube adopts, that, in case the contact-angle is zero, the surface of the meniscus is a hemisphere, and the height of the meniscus equal to the radius of the tube, entirely inadmissible, but even the closer approximation, given by Poisson¶, cannot be legitimately applied, except possibly in the one case of water. This approximation is based upon the assumption that the radius of the capillary tube is very small compared with the capillary

<sup>\*</sup> Quincke, Pogg. Ann. cv. p. 1 (1858). † Magie, Wied. Ann. xxv. p. 434 (1885).

<sup>†</sup> Traube, Jour. für prak. Chem. xxxi. p. 514 (1885). \$ Laplace, Méc. Cél. vol. iv., Suppl. to 10th Book, p. 63.

<sup>¶</sup> Ann. Chem. Phar. ccxxiii. p. 49. ¶ Nouv. Th. de l'Act. Cap. p. 110.

constant a. In the experiments with water, given by Dr. Traube, the radius of the tube employed was 1.72 millim., and the value of a may be taken as about 3.87. In the cases of the other liquids employed, for which the value of a is in every case less than that for water, the ratio of the radius to the value of a is almost unity. Clearly in these cases the approximation is no longer applicable. A calculation by Poisson's formulas of the height of the meniscus formed by water in a tube of radius 1.72 millim., gives as that height 1.51 millim. The height observed by Dr. Traube was 1.45 The agreement of the calculated and observed results is such that the difference may be explained as due, perhaps, partly to the difficulty of observation noticed by Laplace, partly to the inadequacy of the approximation in tubes of such a diameter, and not necessarily to the existence of a finite contact-angle. The diminution in the height of the meniscus as the temperature rises may be explained from the wellknown fact that the value of  $a^2$  decreases as the temperature rises, and does not demonstrate the existence of a variable contact-angle.

Method.—The method employed in the investigation here presented was, in general, that used by Prof. Quincke\*. It consists in the comparison of the values of  $a^2$ , for the different liquids examined, determined by two independent methods. One of the methods is independent of any assumption about the contact-angle, and the other involves the assumption that the contact-angle is zero. The formulas show that, in case this assumption is untrue, the value of  $a^2$  given by the latter method should be less than that given by the other; while the results of the two methods should be in substantial agreement if the assumption is justifiable.

Both methods employed were based upon measurements of the dimensions of large air-bubbles formed in the liquid under a horizontal glass plate. In the first method the distance measured was the vertical distance from the bottom of the bubble to the horizontal plane containing the greatest section of the bubble. This distance, in the subsequent formulas and tables, is called q. In the second method the distance measured was the vertical distance from the bottom of the bubble to the horizontal plane containing the circle in which the bubble-surface is in contact with the glass plate. This distance is called k. In both cases a measurement of the diameter of the greatest horizontal section of the bubble, designated by l, was

<sup>\*</sup> Pogg. Ann. exxxix. p. 1 (1870).

made for use in the correction-terms of the formulas; and for use in the second method, an estimate of the difference between that diameter and the diameter of the circle of contact of the bubble with the glass was also necessary. The contact-angle  $\omega$  was assumed to be 0.

The formulas used in the computation of  $a^2$  from these measurements are slight modifications of those given by Poisson\*. They are

$$a^2 = q^2 + \frac{2qa^2}{\mu} - \frac{a^3}{3l}(2\sqrt{2}-1), \quad . \quad . \quad . \quad . \quad (I.)$$

$$a = \frac{k}{\sqrt{2}\cos\frac{\omega}{2}} + \frac{a^2}{\mu\sqrt{2}\cos\frac{\omega}{2}} - \frac{a^2}{3l\sqrt{2}\cos^2\frac{\omega}{2}} \left(1 - \sin^3\frac{\omega}{2}\right). \text{ (IIa.)}$$

Formula (II a), on the supposition that  $\omega = 0$ , becomes

$$a = \frac{k}{\sqrt{2}} + \frac{a^2}{\mu\sqrt{2}} - \frac{a^2}{3l\sqrt{2}}$$
. . . (IIb.)

In these formulas  $\mu$  denotes the radius of curvature at the centre of the under surface of the bubble. Since the bubbles used were in every case so large that their under surfaces could be considered plane, the term containing  $\mu$  could be neglected in both formulas. The computation is made in both cases by using the value of  $a^2$  given by the first term of the formula in the calculation of the correction-term. One such

approximation is usually sufficient.

Apparatus.—The liquids examined were contained in a tank, about 25 centim. square, formed of heavy plates of plate glass, mounted in an iron frame furnished with levelling screws. The tank and all parts of the apparatus that came in contact with the liquids were carefully cleaned, first with dilute nitric acid, next with a mixture of alcohol and a strong solution of caustic potash, and lastly, with dilute hydrochloric acid. They were also repeatedly washed under the tap, and finally rinsed with distilled water. As this process was tedious and did not seem to be in every case necessary, washing with alcohol and ether was sometimes substituted for it. bubble was formed, in a way kindly suggested to me by Mr. Worthington and recommended by Gauss †, under the slightly concave face of a plano-concave lens. The lens was placed on three small porcelain supports, and the liquid poured in until its level was above the lower surface of the lens, yet so that the upper plane surface of the lens was not covered.

<sup>\*</sup> Nouv. Th. de l'Act. Cap. p. 217. † Gauss, Fig. Fluid., Werke, vol. v. p. 77.

The bubble was blown from a glass pipette. By means of the levelling-screws of the tank the bubble could readily be placed central under the lens. Its horizontal section appeared always to be strictly circular. The curvature of the lens' surface was such that bubbles with diameters ranging from 25 millim. to 150 millim. could be examined. In all the experiments the liquids seemed to readily and completely wet the lens, and the bubbles formed moved freely and without distortion for slight

changes of the levelling-screws. The tank stood on a heavy slate slab mounted on a levelling-To the slab was cemented a plane plate of plate glass, which was set horizontal by means of the levelling-screws of the table. Upon this plate slid freely a smaller plate of glass carrying a pair of Y's, in which rested a microscope. By reversals and adjustments of the Y's, the axis of the microscope was placed horizontal. The microscope carried a 4-inch object-glass, and was furnished with an eyepiece-micrometer. The arrangement was, in fact, a simple microscope-cathetometer\*. With it the measurements of the distance q were made. At about two or three metres from the tank, and at the same level as the bubble, the collimator of a spectroscope was set up with the slit horizontal, and illuminated by a gasflame or by an incandescent electric lamp. An image of the slit was formed by reflexion at the surface of the bubble, along the line in which that surface was met by the greatest horizontal section. The position of this image was determined by the eyepiece-micrometer. Slight variations in the height of the slit made no measurable changes in the apparent position of the image. To enable the position of the bottom of the bubble to be determined, use was made of a fine glass index or pointer. This was carried in a clamp attached to the tank, and could be moved vertically by means of a fine screw until its point came in contact with the bottom of the bubble. The position of the point of contact could be very exactly determined by the eyepiece-micrometer from the apparent contact, at that point, of the pointer and of its image reflected from the surface of the bubble. The distance from the image of the slit to the point of contact of the pointer, measured by the eye-piece micrometer, is the distance q.

The measurements of the distance k were made by a method which I have elsewhere described  $\dagger$ . A vertical microscope mounted on an arm carried on the sliding piece of a cathetometer was placed so as to be as nearly as possible over the centre of the lens and of the bubble. On the face

<sup>\*</sup> Quincke, Pogg. Ann. cv. p. 1 (1858).

<sup>†</sup> Amer. Journ. Science, xxxi. p. 189 (1886).

of the object-glass was fastened a small piece of white paper, the images of which, reflected at the under surface of the lens and at the surface of the bubble, could be observed by the microscope. The paper was illuminated by the rays from a gas-flame or an incandescent electric lamp, concentrated by a lens and reflected upon the paper by a mirror. The mirror was a glass plate, silvered on the front surface, backed with black paper, and pierced with a small hole through which the reflected images were observed. Light was thus largely excluded from the interior of the bubble. The cathetometer was furnished with a micrometer-screw reading directly to hundredths of a millimetre. To make a measurement of k a bubble was formed under the lens, and observations were suspended until the liquid film had evaporated from the centre of the lens under the microscope. Five settings were then made on the sharply focused image of the paper reflected at the under surface of the lens, and five settings on the image reflected at the bottom of the bubble. The distance between the two positions, determined from the means of these settings, is the distance A-N of formula III. which To form a new bubble, most of the air contained in the one already measured was removed with the pipette, yet not so much that the liquid again wetted the portion of the lens under the microscope. The bubble was then enlarged by the introduction of more air. In this way the delay occasioned by waiting for the evaporation from the lens' surface was avoided, and an accuracy in the settings obtained which was not possible when the reflexions were observed before the reflecting portion of the lens became dry.

Calculation of k from Measurements.—If the measurements described were made upon a bubble formed under a plane glass plate, it can easily be shown that the measured distance A-N would be the desired distance k. Since, however, the bubble is formed under a lens, three corrections are

necessary:

1. The first of these arises from the fact that in the first observation the rays from the object pass through the thick lens, are reflected at a convex surface, and pass out through the lens. If we express by

A, the distance from the object to the lens in the first observation,

e, the thickness of the lens at its centre,

n, the index of refraction of the glass, and by

f, a distance such that (n-1)  $f = \mathbb{R}$ , the radius of curvature of the concave face of the lens,

it may be easily shown that the distance in air from the object mounted on the end of the object-glass to a point seen clearly and in good focus, which distance, in this method of observation, is taken as a constant, is expressed by

$$2A + 2e - \frac{2n}{n-1} \cdot \frac{(A+e)^2}{f}$$

2. The second correction arises from the fact that in the second observation the rays from the object pass twice through the thick lens, once before and once after reflexion at the surface of the bubble. By the use of the formulas given by Gauss\*, if we represent further by

N, the distance of the object from the lens in the second observation, and by

h, the distance from the centre of the concave surface of the lens to the bottom of the bubble,

we may express the same constant distance between object and sharply focused point by

$$2\mathbf{N}+2e+2h+\frac{2\mathbf{N}(e+2h)+(e+2h)^2}{f}.$$

This expression is an approximation obtained by neglecting terms containing the second and higher powers of N/f.

From these formulas the value of h is found to be

$$h = A - N - \frac{n}{n-1} \cdot \frac{(A+e)^2}{f} - \frac{N(e+2h) + \frac{1}{2}(e+2h)^2}{f}$$
. (III.)

3. To obtain the value of k, the value of h must be diminished by the distance from the centre of the concave face of the lens to the horizontal plane containing the circle of contact. This is the height of the arc of which the chord is the diameter of the circle of contact. This diameter was found by diminishing the measured diameter of the greatest horizontal section of the bubble by a constant found by observation for each liquid.

To calculate these corrections a knowledge is necessary of the thickness and index of refraction of the lens, and of the radius of curvature of its concave face. The thickness of the lens used in the experiments was determined with a spherometer to be 7.859 millim. The index of refraction of the lens was found from its polarizing-angle to be 1.539. By the use of the concave face as a mirror, its radius of curvature

<sup>\*</sup> Gauss, Diop. Unters., Werke, vol. v. p. 261.

was determined to be 3742 millim. The value of A is 14.63 millim., and the value of N is found from it when A-N has been measured. From these quantities the first correction was computed once for all to be 0.160 millim. The second correction varies with each value of h; it may be calculated by the use of the approximate value for h obtained by omitting the second correction. Its value differs for different liquids. but varies so little for any one liquid that, after it has been calculated for one bubble, it may be estimated for the others. It usually amounts to between 0.03 and 0.04 millim. the third correction a table was prepared giving the heights of the arcs for a series of values of chords such as those ordinarily obtained in the experiments, and the corrections were obtained by interpolation. This correction was the one of most importance, its values ranging from 0.3 millim. to 0.7 millim.

In the computation of  $a^2$  from the value of k thus obtained, the value of  $\omega$ , the angle made by the surface of the bubble with the horizontal plane passing through the circle of contact, was assumed to be zero, although strictly it should have been taken to be the angle made with that plane by the lens' surface at the circle of contact. The cosine of that angle was so nearly equal to unity that the slight difference was neglected.

## RESULTS.

The results obtained by the use of the above described methods of measurement are presented in the following tables. The first column contains the values of q, expressed in divisions of the eyepiece-micrometer. One division of this micrometer was found, by comparison with a Roger's stage-micrometer, to be equal to 0.02658 millim. second column contains the values of A-N in millimetres, A and N being each positions determined by the mean of five settings of the micrometer-screw of the cathetometer. The third column contains the computed values of k; the fourth the semidiameters of the bubbles in millimetres; the fifth and sixth the values of  $a^2$ , computed from q and from k respectively. The constant of diameter given is the length to be subtracted from the measured semidiameters to obtain the semichords used in the computation of the third correction for k. The temperatures of the liquid and of the air just above the liquid are also given sufficiently often to indicate their values during a set of observations. The temperatures are put together in brackets, the upper one being the temperature of the liquid.

Distilled Water. March 7, 1888.
Specific density 1.0. Constant of diameter 1.2 millim.

q.	A-N.	k.	7.	$aq^2$ .	$ak^2$ .	T.
150·5 149·75	6·137 6·310	5·550 5·580	54 64	15·28 15·26	14·87 15·11	
150·25 152·5	6:063 6:081	5·434 5·493	58·75 57·7	15·28 15·72	14.29	
149·5 148·75 147·8	6·081 6·045 6·213	5.478 5.376	55 53·5 70	15·10 14·93 14·91	14·58 14·49 14·08	
148·2 149·2 148·5	6·406 5·985 5·964	5·513 5·382 5·452	73 56 49·5	15.00 15.04 14.82	14·80 14·01 14·32	
149.3	6.136	5.472	60	15.11	14.59	$\left\{egin{array}{l} 2\overset{\circ}{2}\cdot 5 \ 26 \end{array} ight.$

Omitting the first four bubbles, the large results from which are probably owing to a lower temperature at the beginning of the observations, the means of the remaining seven are  $a_q^2$  14.99 and  $a_k^2$  14.41.

Probable errors of means  $\begin{cases} a_q^2 & 0.025 \\ a_k^2 & 0.068. \end{cases}$ 

The same. April 3, 1888.

q.	A-N.	k.	l.	$a_q^2$ .	$ak^2$ .	T.
146.9	6.161	5:481	61	14.62	14:57	$\begin{cases} 2\mathring{1} \cdot 6 \\ 23 \cdot 0 \end{cases}$
147·5 147·9	6·105 6·134	5·489 5·486	57 59	14·73 14·82	14.57 $14.57$	
147·2 147·8	6·239 6·004	5·500 5·445	64·5 53	14·75 14·73	$14.70 \\ 14.32$	$\left\{\begin{matrix} 21.8\\23.6 \end{matrix}\right.$
147·9 148·0 146·9	6·119 6·279 6·063	5·487 5·479 5·469	58 68 55·5	$14.81 \\ 14.92 \\ 14.56$	14·57 14·61 14·46	∫ 22·9
147·2 147·0	6·280 6·195	5·472 5·491	68·5 62·5	14·78 14·68	14·58 14·64	₹ 24.5
147·2 146·8	6·018 6·117	5·445 5·461	54 59·5	14·64 14·61	14.32 $14.46$	{ 23.6 25.3
			Means	14.72	14.53	

Probable errors of means  $\begin{cases} a_q^2 & 0.018 \\ a_k^2 & 0.022. \end{cases}$ 

Ethyl-Alcohol (Squibb's Absolute). March 10, 1888. Specific density 0.793. Constant of diameter 1.5 millim.

q.	A-N.	k.	l.	$a_q^2$ .	$a_k^2$ .	T.
90·0 89·5 91·2 90·0 91·0 90·0 90·5 91·5 91·5 91·0 90·8	4·024 4·001 3·867 4·270 3·921 4·155 3·947 3·857 4·120 3·936 3·972	3·369 3·321 3·463 3·337 3·285 3·474 3·417 3·370 3·440 3·378 3·392	60·5 62 52 69·5 59·25 62 52 48·75 62 54 55·5	5·584 5·526 5·601 5·708 5·704 5·587 5·622 5·733 5·772 5·690 5·670	5·570 5·420 5·420 5·452 5·295 5·920 5·712 5·551 5·803 5·589 5·636	$\left\{ egin{array}{cccccccccccccccccccccccccccccccccccc$
90.5	3.997	3:402	56.5 Means	5.630	5·669 	{ 23.2

Probable errors of means  $\begin{cases} a_q^2 \ 0.013 \\ a_k^2 \ 0.035. \end{cases}$ 

The same. April 6, 1888.

q.	A-N.	k.	ī.	$a_q^2$ .	$ak^2$ .	T.
89·3 89·7 89·4 88·3 90·2 87·9 88·8 88·0 89·9	4·065 3·973 4·001 4·138 3·911 4·001 3·981 4·053 3·983	3·439 3·365 3·421 3·366 3·359 3·362 3·348 3·372 3·418	59 57·5 55·5 67·5 53·5 59·5 59 62 54·5	5·495 5·539 5·498 5·390 5·590 5·327 5·434 5·344 5·556	5·774 5·526 5·706 5·540 5·497 5·516 5·469 5·559 5·697	$ \begin{cases} 2\overset{\circ}{4} \cdot 2 \\ 26 \cdot 4 \end{cases} $ $ \begin{cases} 24 \cdot 8 \\ 27 \cdot 1 \end{cases} $
88·9 89·5	4·021 3·975 4·221	3·392 3·366 3·348	58·75 57·5 73 Means	5·445 5·515  5·467	5·611 5·530 5·493 5·576	$\begin{cases} 25.4 \\ 27.3 \\ \end{cases}$

Probable errors of means  $\begin{cases} a_g^2 \ 0.017 \\ a_k^2 \ 0.018. \end{cases}$ 

The same. April 23, 1888.

q.	A-N.	k.	ι.	$a_q^2$ .	$a_{k}^{2}$ .	T.
90·15 90·2 90·5 90·45 90·2 90·45	4·028 4·089 4·028 4·060 4·214 4·047	3·402 3·439 3·428 3·379 3·396 3·443	58·5 60 56·75 62 70 57	5·591 5·607 5·636 5·642 5·627 5·631	5·674 5·798 5·755 5·612 5·674 5·798	$   \begin{cases}                                  $
90·55 90·5 90·3 90·3 90·2	4·024 4·050 4·141 4·038 4·095	3:450 3:410 3:436 3:428 3:455	55 59·5 63·5 57·5 59·5	5·637 5·642 5·627 5·612 5·606	5·818 5·707 5·794 5·755 5·852	{ 19·5 20·5
90.15	4.056	3.446	57·5 Means	5·589 5·621	5·823 5·755	$\begin{bmatrix} \frac{20}{21} \\ \end{bmatrix}$

The same. April 24, 1888.

q.	A-N.	k.	ī.	$aq^2$ .	$a_k^2$ .	T.
89·8	4·029	3·366	61	5·560	5·570	$ \begin{cases} 1\mathring{7} \cdot 8 \\ 18 \cdot 7 \end{cases} $ $ \begin{cases} 19 \\ 20 \end{cases} $ $ \begin{cases} 19 \cdot 6 \\ 20 \cdot 3 \end{cases} $
90	4·039	3·352	62·5	5·585	5·532	
90·3	4·011	3·339	61·5	5·625	5·494	
90·1	4·074	3·387	62·5	5·597	5·645	
89·1	4·050	3·294	66·5	5·486	5·336	

Chloroform. March 31, 1888. Specific density 1·482. Constant of diameter 1·5 millim.

q.	A-N.	k.	l.	$aq^2$ .	$a_k^2$ .	T.
73·2 71·3 74·8 73·5 74·3 74·0 71·3 72·0	3·344 3·478 3·292 3·323 3·246 3·316 3·653 3·617	2·729 2·764 2·696 2·705 2·715 2·748 2·775 2·729	58 64·5 57 58·5 52·5 55 73·5	3·708 3·527 3·868 3·739 3·811 3·783 3·535 3·603	3·663 3·764 3·576 3·606 3·625 3·713 3·802 3·675	$ \begin{cases} 2\overset{\circ}{2} \\ 26 \end{cases} $ $ \begin{cases} 23 \cdot 2 \\ 26 \cdot 3 \end{cases} $ $ \begin{cases} 24 \\ 26 \cdot 7 \end{cases} $
			Means	3.697	3.678	

Probable errors of means  $\begin{cases} a_q^2 \ 0.027 \\ a_k^2 \ 0.017. \end{cases}$ 

Acetic Acid (No. 8). April 2, 1888. Specific density 1.038. Constant of diameter 1.2 millim.

q.	A-N.	k.	. <i>l</i> .	$a_q^2$ .	a <sub>k</sub> <sup>2</sup> .	T.
112.2	4.772	4.143	58	8.613	8:376	{ 18.6
112.6 111.6 111.5	4.684 4.810 4.795	4·093 4·172 4·111	56 59 62	8·664 8·528 8·511	8·174 8·497 8·265	ſ 20·2
112·0 112·5 111·8	4·804 4·712 4·881	4·167 4·135 4·128	59 55 66	8·589 8·644 8·587	8·474 8·341 8·347	20.2
112·1 111·7	4·712 4·767 4·843	4·128 4·115 4·141	55·5 60 63	8·586 8·547 8·500	8·311 8·277 8·387	∫ 21.6
111:3	4 843	4 141	Means	8.577	8.345	23.2

Probable errors of means  $\begin{cases} a_q^2 & 0.011 \\ a_k^2 & 0.019. \end{cases}$ 

Methyl-Alcohol. April 5, 1888.

Specific density 0.812. Constant of diameter 1.5 millim.

q.	A-N.	k.	ī.	$a_{q}^{2}$ .	a <sub>k</sub> <sup>2</sup> .	T.
95.2	4.180	3.505	61.5	6.242	6.022	$\left\{ \begin{matrix} 19.6 \\ 23 \end{matrix} \right.$
94·6 92·8 94·6	4·177 4·233 4·081	3·532 3·499 3·487	59·75 65 56·5	6·159 5·943 6·159	6·116 6·012 5·958	
93·9 93·6 93·3	4·322 4·108 4·167	3·564 3·514 3·517	66.5 56.5 60	6·086 6·022 5·994	6·240 6·047 6·066	${20.8 \atop 23.8}$
92·4 93·3 94·2	4·287 4·124 4·168	3·502 3·543 3·503	68 55.5 61	5·899 5·982 6·111	6·027 6·140 6·017	
94.0	4·103 4·183	3·480 3·543	58·5 59·5	6·079 5·993	5·939 6·150	$\left\{ egin{array}{l} 21.6 \ 24 \end{array}  ight.$
			Means	6.056	6.061	

Probable errors of means  $\begin{cases} a_q^2 & 0.019 \\ a_k^2 & 0.016. \end{cases}$ 

Formic Acid (commercial). April 7, 1888. Specific density 1.148. Constant of diameter 1.0 millim.

q.	A-N.	k.	Z.	$aq^2$ .	$a_{k}^{2}$ .	.T.
102.3	4.562	3.856	63	7.215	7.279	\{\rightarrow{\circ}{24.6}\rightarrow{\circ}{\circ}
99·3	4·40·1	3·747	60	6·778	6·875	$\left\{ egin{array}{l} 23.2 \\ 24.5 \end{array} \right.$
103·2	4·585	3·845	65	7·329	7·247	
99·9	4·387	3·753	58·5	6·855	6·901	∫ 23·6
103·6	4·611	3·860	65·5	7·387	7·301	
99·3	4·315	3·720	56	6·775	6·775	
103·9	4·623	3·854	66·75	7·432	7·284	\ 24.6
101·5	4·420	3·779	59	7·074	6·991	
103·45	4·585	3·878	63	7·361	7·360	∫ 24·4
103·5	4·586	3·879	64	7·368	7·361	
100·5	4·340	3·758	55	6·939	6·907	
			Means	7:137	7.117	25.3

The variations in the results show changes in the value of  $a^2$ , and hence the probable errors of the means were not calculated.

Turpentine. April 9, 1888.

Specific density 0.863. Constant of diameter 1.0 millim.

a.	A-N.	ķ.	l.	$aq^2$ .	$a_k^2$ .	T.
96.5	4.369	3.602	66.5	6.423	6.370	{ 17.4 19.6
96·8 96·35 97·2	4·210 4·227 4·133	3·592 3·561 3·588	57·5 60·5 52·5	6·444 6·388 6·474	6·320 6·220 6·290	
97·05 97·05 96·55	4·239 4·424 4·163	3·557 3·558 3·567	61·5 72 56	6·476 6·508 6·400	6.200 $6.225$ $6.225$	$\left\{ \begin{matrix} 19.6 \\ 21.2 \end{matrix} \right.$
96·45 97·0 96·2	4·229 4·323 4·352	3·555 3·584 3·593	61 65 66	6·403 6·486 6·383	6·195 6·300 6·335	
96.45	4.193	3.584	57	6.391	6.290	$\left\{ \begin{smallmatrix} 21\cdot 0\\ 22\cdot 1 \end{smallmatrix} \right.$
			Means	6.434	6.270	

Probable errors of means  $\begin{cases} a_q^2 & 0.009 \\ a_k^2 & 0.012. \end{cases}$ 

Petroleum (refined). April 9, 1888. Specific density 0.782. Constant of diameter 1.0 millim.

q.	A-N.	k.	l.	$a_q^2$ .	a <sub>k</sub> 2.	T.
100·5 99·3 98·6 99·4 99·25 98·65 98·5 98·85 99·2	4·305 4·440 4·292 4·267 4·465 4·257 4·265 4·274 4·135	3·648 3·638 3·687 3·626 3·636 3·617 3·601 3·590	60 68·5 56·5 59 70 59 60·5 60·5 52·5	6.940 6.801 6.673 6.789 6.798 6.688 6.672 6.719 6.738	6·518 6·497 6·620 · 6·447 6·497 6·421 6·366 6·396 6·295	\[ \begin{aligned} 20\cdot 8 \\ 22\cdot 2 \\ \end{aligned} \\ aligned
99·2 99·85 98·75	4·132 4·243 4·250	3·622 3·602 3·615	50 59 58·5 Means	6·728 6·849 6·701 6·758	6·401 6·355 6·406	

Probable errors of means  $\begin{cases} a_q^2 & 0.015 \\ a_k^2 & 0.016. \end{cases}$ 

Benzine. April 11, 1888.

Specific density 0.698. Constant of diameter 1.0 millim.

q.	A-N.	k.	ī.	$a_q^2$ .	a <sub>k</sub> <sup>2</sup> .	T.
91.75	4.013	3.396	57.5	5.792	5.650	$\begin{cases} 19.2 \\ 20.2 \end{cases}$
91·1 89·8	4·058 4·130 4·026	3·403 3·417 3·423	60 63·5 56·5	5.693 5.566 5.716	5.679 5.731	
91·15 90·85 90·85	4·055 4·016	3·438 3·399	57·5 57·5	5·681 5·681	5·741 5·794 5·660	$\left\{ \begin{array}{l} 20 \\ 21 \end{array} \right.$
89·8 91·3	4·088 4·023	3·432 3·393	60 58·5	5·561 5·739	5·770 5·636	{ 20·2 21·5
			Means	5.678	5.707	

Probable errors of means  $\begin{cases} a_q^2 & 0.018 \\ a_k^2 & 0.016. \end{cases}$ 

Ether. April 11, 1888.

Specific density 0.725. Constant of diameter 1.0 millim.

q.	A-N.	k.	l.	$aq^2$ .	$a_k^2$ .	T.
84·0 85·55 84·3	3·848 3·759 4·002	3·151 3·156 3·165	62·5 56·5 70·5	4·875 5·043 4·923	4·880 4·889 4·933	{ 19·2 { 21·5
84.65 85.15 84.65 85.45 85.5	3·736 3·696 3·848 3·768 3·705	3·120 3·102 3·151 3·129 3·153	57.5 55 62.5 59 53	4·940 4·993 4·950 5·035 5·029	4·779 4·718 4·880 4·809 4·875	\{\frac{19.4}{21.8}
84·75 85·2 85·5 84·6	3·802 3·696 3·795 3·848	3·163 3·138 3·140 3·161	59 53·5 60 62	4·955 4·995 5·039 4·943	4·911 4·827 4·844 4·911	§ 19·4
	5310	0 101	Means	4.977	4.855	1 22

Probable errors of means  $\begin{cases} a_q^2 & 0.010 \\ a_k^2 & 0.011. \end{cases}$ 

Sources of Error.—Before discussing the bearing of these results upon the question of the existence of a finite contactangle, it is important to consider the possible sources of constant error in a set of observations. These mostly affect the measurement of q. If the tank is so placed that the wall through which the observations are made is not vertical, or nearly so, the distance measured by the microscope and the value of q deduced from it will be a little too small. same result will follow if the microscope is not horizontal in its supports. If the microscope does not move in a horizontal plane, the value of q will be in error. A flaw or a series of striæ in the glass wall will also possibly affect a set of observations as a whole; for the limitations as to the size of the bubbles used and the position of the pointer are such that any one set of observations is made practically through the same parts of the wall of the tank.

The value of k may be measured at less than its true value if the vertical microscope is not placed over the centre of the lens. It is, however, easy to set it so that the error shall not exceed one hundredth of a millimetre. An error in the estimation of the constant of diameter also introduces an error in the determination of k. The estimation would have, however, to be in error by 2.5 millim. in order to explain the smallest

differences from which the existence of a contact-angle is inferred.

The variations in single readings of the value of q arise partly from the fact that the image of the slit is not all in focus at once, and spreads out at the ends. It is sometimes difficult to avoid setting on a wrong portion of the image, especially after the field has been illuminated to enable the eyepiece-micrometer to be read. The proper illumination of the pointer also offers difficulties, which may result in some cases in faulty focusing and consequent errors of setting. The readings of k are made uncertain from the adaptability of the eye. The faintness of the reflected images makes it impracticable to use the method of determining the focus by the parallax of the image with a spider-line in the eyepiece. In the five settings from which a position was determined, the extreme readings of the micrometer-screw differed usually by three or four hundredths of a millimetre.

Criterion of the Existence of a Contact-angle.—Although these sources of error, and possibly real differences in the values of  $a^2$  for different bubbles in the same liquid, render the separate results in a series sometimes widely discrepant, and the small number of results included in the mean seems to make the ordinary rules for obtaining the probable error scarcely applicable, yet I have thought it worth while to append to the means their probable errors. I think that the probability of constant errors of importance is slight, and the accuracy of the observations sufficient to warrant the belief. when the results by the two methods differ by more than the sums of their probable errors, that the difference is a real one. In all cases but that of alcohol, the difference, when it exists, is such that the result by the "k" method is less than that by the "q" method. In these cases I have concluded that the observations indicate a finite contact-angle.

Water.—The results for water point, though doubtfully, toward a finite contact-angle. The difference between the "q" and "k" values in the first set of observations is very striking. The difference in the second set is much less, but still evident. The large difference in the first set may perhaps be explained by the difference of temperature between the water and the air, as discussed later in this paper. From the second set of observations alone I should hardly be willing to draw the conclusion of a finite contact-angle for water, if it were not that the results of these observations are substantiated by those of a number of preliminary measurements. By a modification of the "q" method, in which "q" was observed by an ordinary cathetometer, I obtained  $a^2$  equal to

15.28 at 21°.5, and again 15.39 at 16°.7, and, by the method of this paper, 15.17 at 23°.2. The values of  $a^2$  obtained on the same days by the "k" method, in the first two cases with bubbles formed under a flat plate, and in the third under the lens as described, are respectively 15:18, 14:93, and 14:96. The evidence afforded by these consistent differences of the results by the two methods is strengthened by the fact that experiments on the rise of water in capillary tubes by Gay-Lussac\*, Frankenheim and Sondhaust, and Brunnert, give for a<sup>2</sup> at 20° the value 14.80, and those of Volkmann give 14.90. Assuming that the "q" values are correct, these values are such as would follow from the method of capillary tubes if there were a small finite contact-angle, and if in the computations the contact-angle were assumed to be zero. The differences in the values of  $a^2$  are, however, so small, and the difficulty of obtaining surfaces of glass really clean so great, that, while these experiments point to a finite contactangle between water and glass as probable, yet I do not feel

that they demonstrate its existence.

Ethyl-Alcohol.—The results for ethyl-alcohol have been presented fully, although those of April 6 and April 23 evidently contain some error. I am satisfied that the magnitude of the "k" results on those days is not due to any constant error of observation, and suggest the following as its probable explanation. The observations of those days were made, as has been described, after the centre of the lens' surface was cleared of liquid by evaporation. It seems to me probable that, owing to evaporation at the circle of contact, in the way discussed later, the water taken up by the alcohol from the air blown into the bubble was left behind on the lens by the more rapid evaporation of the alcohol, as explained by Prof. J. Thomson, and that there was thus formed in the upper portion of the surface of the bubble a film of liquid with a higher surface-tension than that of the pure alcohol. The bubble was thus made higher than it would have been if the surfacetension had been throughout that of pure alcohol, and the value of a<sup>2</sup>, calculated from its height, was greater than the true value. Since precipitation of alcohol-vapour was going on upon the cooler lower surface of the bubble, that portion of the bubble was not similarly affected, and the constant obtained by the "q" method was that of pure alcohol. This explana-

<sup>\*</sup> Laplace, Méc. Cél. Suppl. à la Th. de l'Act. Cap. p. 54.

<sup>†</sup> Pogg. Ann. lxxii. p. 211 (1847). † Berlin Berichte, 1846, p. 181. § Wied. Ann. xvii. p. 353 (1882).

<sup>|</sup> Maxwell, 'Theory of Heat,' p. 293.

tion is supported by the observations of March 10 and April 24. The measurements were then made while the film of liquid still covered the lens' surface, so that the supposed irregularities at the circle of contact were far less likely to occur. The settings were more difficult and the readings not quite so accordant, but the agreement of the results by the two methods is such as to indicate that the cause of the discrepancy in the

results of the other days was not operative.

This view obtains further support from the results of another series of measurements on ethyl-alcohol\*. By the "q" method the value then obtained for  $a^2$  was 5.576 at 23°. By the "k" method, in which the bubbles were formed under a flat plate, the values were 5.803 and 5.786 at 22°. From the ordinary method by the use of capillary tubes the value was 5.805; and by a method in which the radius of curvature of the meniscus in a capillary tube was measured directly, and which did not involve the contact-angle  $\dagger$ , the value was 5.859. In the last two methods the disturbing effect of the water in the surface-film would be felt as well as in the "k" method. Hence arises, I think, the substantial agreement of the results by the last three methods, and also the difference between them and the results by the "q" method.

The results of March 10 offer no evidence of a finite contactangle; and though those of April 24 differ by more than one per cent., yet this difference is mostly due to the values given by the last bubble. If these be omitted, the means from the four others are 5.592 and 5.560. The difference is too slight

to demonstrate the existence of a finite contact-angle.

Other Liquids.—In the cases of chloroform, methyl-alcohol, formic acid, and benzine, the agreement of the results is such as not to indicate a finite contact-angle. The variations of the values of  $a^2$  in the case of formic acid, and the way in which those variations were shown by both methods of obser-

vation, are worthy of notice.

In the cases of acetic acid, turpentine, petroleum, and ether, the results indicate the existence of a finite contact-angle. A rough calculation of the value of that angle was made in each case by taking the value of k which would give the mean value of  $a^2$  given by the "k" method, and using it with the mean value of  $a^2$  given by the "q" method to calculate the value of  $\omega$  from formula II  $\omega$ . In the numerical values thus obtained little confidence can be placed. They are only given as rough approximations. The results are collected in the following table:—

<sup>\*</sup> Magie, Proc. Am. Ass. New York, 1887, p. 79. † Magie, Wied. Ann. xxv. p. 421 (1885).

Angle zero.	Angle finite.			Value of $\omega$ .
Ethyl-alcohol.	Water (?)			Small.
Methyl-alcohol.	Acetic acid			20°.
Chloroform.	Turpentine	٠		17°.
Formic acid.	Petroleum			26°.
Benzine.	Ether .			16°.

Discussion of the Results.—The close agreement of the "q" and "k" results in those cases in which no finite contactangle is inferred, by showing the general validity of the method of experimentation, is such as to force me to rely with some confidence on the evidence of the existence of a finite contact-angle in the other cases. It is more difficult to decide if this contact-angle is due to the relations among the molecular forces in equilibrium at the line of contact, as was assumed, in the statement of the problem, would be the case. Another possible explanation may be given, in favour of which the experiments here presented offer some evidence. In experiments conducted on the plan here described, the temperature of the liquid is almost necessarily a little lower than that of the air above the lens. Presumably the lens, the upper surface of which is not covered by the liquid, is also at a slightly higher temperature than the liquid. The evaporation from its under surface will therefore be more rapid than from the cooler lower surface of the bubble. the interior of the bubble has become saturated with the vapour of the liquid, evaporation will go on from the lens and precipitation will occur upon the surface of the bubble. This evaporation will cut away the thin liquid surface at its line of contact with the glass; and unless the facility with which the liquid travels over glass is such that new particles move up to completely supply the deficiency, there will not be perfect replacement of the surface, and it will meet the glass with a finite contact-angle. The marked difference between the "q" and "k" results of March 7 for the values of  $a^2$  for water, indicating a large contact-angle, taken in connexion with the large difference between the temperature of the water and that of the air, points towards the explanation just given as a possible one. The liquids, too, for which no finite contact-angle was indicated are either not very volatile or are extremely mobile, and bubbles formed in them move freely under the lens. Bubbles in those liquids for which a finite contact-angle appears are, in every case except that of ether. much less free in their movements under the lens. extreme volatility of the ether may explain the presence of

the finite contact-angle found for it, notwithstanding its great

mobility.

It must be admitted, however, that the temperature differences assumed in the preceding explanation are, for some of the liquids, very slight, especially for those, like turpentine and petroleum, for which the results indicate large contactangles. On the whole, I am inclined to believe that the finite contact-angles indicated are due to the relations among the molecular forces at the line of contact. If this view be accepted, we might assign a limit to the molecular forces between the molecules of glass and those of the liquids for which the finite contact-angle appears, by the help of Gauss's hypothesis as to the similarity in form of the force-functions representing the forces between liquid elements and between liquid and solid elements. Doubt is, however, thrown on that assumption by the values of  $a^2$  obtained for the liquids examined.

Law of Molecular Force.—The expression for the force between two elements of a liquid is, in Laplace's and Gauss's theories,  $D^2 f(x) dv^2$ , where D represents the density of the liquid, dv the volume of an element, and f(x) a function of the distance x between the elements. In the operation by which Laplace's capillary constant  $H = a^2D$  is determined in terms of f(x), the only property of this function of which use is made is that it diminishes with extreme rapidity as the distance x increases, and becomes insensible for measurable values of x. No assumption is made as to whether it is the same for all kinds of molecules. In Gauss's discussion of the contact-angle he makes the assumption, to which reference has already been made, that the two functions f(x) and F(x), the one of which is proportional to the force between two elements of the liquid separated by the distance x, and the other proportional to the force between an element of the liquid and one of the solid, are in a ratio independent of x; that is, that they have the same form. If this assumption be true for the relation between these forces, it seems likely that it would be true for the different values of f(x) for different liquids. Indeed, if the molecular force varies inversely as some power of the distance, it seems the most probable supposition that this power is the same for all liquids. If this were so, the integral  $\int z dz \psi(z)$  contained in the expression for the capillary constant H, since  $\psi(z)$  is a function ultimately depending on f(x), should then be the same for all liquids. Since H equals  $2\pi D^2 (zdz\psi(z))$ , the values of H/D<sup>2</sup> for different liquids should be constant. In the following table are presented the values of  $a^2$ , D, H, and  $H/D^2$ :—

Chloroform		a <sup>2</sup> . D.	н.	H/D2.
Methyl-Alcohol         6 056         0·812         4·918         7·458           Formic Acid         7·137         1·148         8·193         6·217           Turpentine         6·434         0·863         5·552         7·458           Petroleum         6·758         0·782         5·285         8·642	Ethyl-Alcohol Chloroform Acetic Acid Methyl-Alcohol Turpentine Petroleum	$\begin{array}{cccc} 5.652 & 0.793 \\ 3.697 & 1.482 \\ 8.577 & 1.038 \\ 6.056 & 0.812 \\ 7.137 & 1.148 \\ 6.434 & 0.863 \\ 6.758 & 0.782 \end{array}$	4 4484 5·479 8·903 4·918 8·193 5·552 5·285	14·99 7·124 2·495 8·263 7·458 6·217 7·455 8·642 8·135

There is no relation among these values of  $H/D^2$  which permits the conclusion that the functions f(x) for different liquids have the same form or are connected by any simple relation. This result shows further that Gauss's hypothesis is probably in error. We are, therefore, precluded from drawing a conclusion, which would otherwise follow from Gauss's equation for the contact-angle, as to the limits within which the molecular forces must lie in case the liquid makes with the solid a finite acute contact-angle.

In conclusion it may be noted that the values of  $a^2$  obtained by the "q" method are probably fairly accurate for the liquids used. As, however, the investigation was not undertaken with the purpose of obtaining these values as physical constants, no especial pains were used to employ liquids which

were chemically pure.

I desire to express my thanks to Mr. Taylor Reed and Mr. A. H. Scofield, Fellows of the College, for the assistance which they have given me in the observations.

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- XX. Maxwell's Theory of the Viscosity of Solids and its Physical Verification. By CARL BARUS, Assistant Geologist, U.S. G. S.\*
- 1. THE viscosity of solids has been theoretically discussed in more or less elaborate memoirs by O. E. Meyer, Boltzmann, Neesen, Warburg, Maxwell, and Butcher. Views of a distinctly theoretical kind have also been given by

<sup>•</sup> Communicated, with the permission of the Director of the U.S. Geological Survey, by the Author.

Weber and Kohlrausch, and more recently by Nissen. In almost all cases, excepting alone Butcher's work \*, which formulates the theory of Maxwell †, the problem has been

approached from distinct points of view.

Despite the diversity of methods of discussion and the elaboration of evidence, the results arrived at do not in any case so fully represent the phenomenon as to lead to general acquiescence in one elementary physical hypothesis. Boltzmann's theory is perhaps the most powerful, and is elegantly worked out; but it is purely mathematical in character. Maxwell's theory has the soundest physical basis, although left by its author in shape merely of a terse verbal sketch.

Now it seems to me, if indeed I may venture on any assertion, that this theory is a version of Williamson's ‡ theory of etherification, and of Clausius's § theory of electrolysis; for viscosity in Maxwell's conception is a phenomenon evoked by certain changes of molecular structure, the inherent nature of which is ultimately chemical. I say chemical, because if molecular break-up occur, cardinal questions at once arise as to the manner of removal of the debris; and the phenomenon thus depends not only on the past history, but on the immediate future history of the typical mean configuration.

The analogy of the three theories is very close, so that they admit of generic classification. They are examples of the invasion of statistical method into liquid and solid molecular

kinetics.

The behaviour of steel when regarded as a viscous solid and in the light of known facts | is convincingly in favour of the

\* Butcher, Proc. Lond. Math. Soc. iii. 1878.

† Maxwell, "Constitution of Bodies," Encyclop. Brit. 9th ed. p. 310, 1876.

† Williamson, Ann. der Chem. und Pharm. lxxvii. p. 37, 1851. § Clausius, Pogg. Ann. c. p. 353, 1857; ibid. ci. p. 338, 1857.

If refer in particular to the work of Dr. Strouhal and myself. Hardness (temper), its electrical and other characteristics, cf. Barus, Phil. Mag. [5] viii. p. 341, 1879; Wied. Ann. vii. p. 383, 1879; Strouhal and Barus, Wied. Ann. xi. p. 930, 1880; ibid. xx. p. 525, 1883. Hardness and magnetization, cf. S. and B., Wied. Ann. xx. pp. 537, 662, 1883. Density and (internal) structure of hard steel and of quenched glass, cf. Barus and Strouhal, American Journ. [3] xxxii. p. 386, 1886; ibid. p. 439; Am. Journ. xxxi. p. 181, 1886. Temper and chemical composition, cf. B. and S., Am. Journ. [3] xxxii. p. 276, 1886. Temper and viscosity, cf. B. and S., Am. Journ. [3] xxxii. p. 444, 1886; ibid. xxxiii. p. 20, 1887; Barus, ibid. xxxiv. p. 1, 1887; ibid. xxxiv. p. 175, 1887. These papers, systematically discussed and enlarged, are embodied with new matter in the Bulletins of the United States Geological Survey, viz.:—Bull. no. 14, pp. 1–226, 1886; Bull. no. 27, pp. 30–61, 1886; Bull. no. 35, pp. 11–60, 1886; Bull. no. 42, pp. 98–131, 1887. Others are forthcoming. The Bulletins can be obtained by addressing the Director of the U.S. Geological Survey.

view to be advocated; and it was the direct bearing of some of the results on Clausius's theory of electrolysis, that led me to suspect a chemical explanation \*, before I became aware of the existence of Maxwell's article. To show how clearly Maxwell's theory interprets the complex and almost anomalous phenomena of viscosity exhibited by tempered steel, is the chief endeavour of the present paper; but I shall also add other matter.

2. It is desirable to pass in brief review the divers hypotheses on the nature of viscosity in solids, to which I have referred.

O. E. Meyer's theory † is the earliest and the most direct. It discusses the action of elastic forces in a medium of imperfect elasticity, and develops formulæ to express the diminution of stress in virtue of the occurrence of internal The results to which Meyer's theory eventually leads are incomplete, and were not fully verified by subsequent experiment. The theory is therefore sharply antagonized by Boltzmann §, by Streintz ||, and by Kohlrausch ¶. In a later paper Meyer \*\* partially assents to these adverse views, acknowledging that the theory does not reproduce the phenomenon actually observed. It also fails, as Kohlrausch (l. c.) pointed out, in predicting an insufficiently slow time of occurrence. After giving reasons for dissenting from Boltzmann's and from Neesen's hypotheses, Meyer proceeds to a partial development of an old hypothesis of Weber ††. This physicist referred viscosity in solids to partial molecular rotation, a view adopted by Kohlrausch ‡‡, by whom it has been more clearly interpreted. The rotations underlying Weber's phenomenon are considered identical with the rotation of molecules postulated by Clausius §§ in discussing

\* Am. Journ. [3] xxxiii. p. 28, 1887. It is much to be regretted that Maxwell's theory was published out of the line of a physicist's usual routine reading.

† Meyer, Pogg. Ann. cli. p. 108, 1874.

† Following the usage of the word by Navier, Cauchy, Poisson, St. Venant, Stokes, Stefan. Cf. Meyer, l. c.

§ Pogg. Ann. Ergänzb. vii. p. 624, 1876. Pogg. Ann. clv. p. 588, 1875; ibid. cliii. p. 405, 1874.

¶ Pogg. Ann. clx. p. 225, 1877. \*\* Wied. Ann. iv. p. 249, 1878.

†† Weber, Pogg. Ann. xxxiv. p. 247, 1835; ibid. liv. p. 1, 1841. ‡‡ Pogg. Ann. cxxviii. p. 413, 1866; cf. also ibid. cxix. p. 337, 1863; ibid. clviii. p. 337, 1876.

§§ Clausius, Pogg. Ann. lxxvi. p. 46, 1849. Shearing stress is referred to: "Wenn ein solcher Körper fremden Kräften unterworfen wird, die von veschiedenen Seiten ungleich auf ihn wirken, er also z. B. nach einer Dimension gedehnt wird, während er nach anderen Dimensionen frei bleibt oder gar zusammengedrückt wird, dann die Moleküle neben ihrer Verschiebung sich auch etwas drehen können, indem sie in Bezug auf ihre Kraftrichtungen den ungleichen Spannungen etwas folgen . . . " (p. 66). certain problems in solid elastics. Following Meyer and others, "elastische Nachwirkung" is a possible occurrence in

liquids.

Boltzmann's \* theory, amplifying deductions of Lamy and of Clebsch, is based on the assumption that the elastic forces are dependent not only on the present but on the preceding deformations of the body. The effect of earlier states of stress on the existing stress diminishes with the intervening time, but is independent of the intervening states of stress. over different viscous deformations are superposable. mann's theory therefore subserves a mathematical purpose, as Kohlrausch† remarked, and, by presupposing the phenomena, brings the laws of solid viscosity tersely into formulæ. If w is an interval of time reckoned back from t to  $t-\omega$  when the strain  $\theta_{t-\omega}$  existed, then Boltzmann's law may be most clearly exhibited, perhaps, in its application to the problem of vibration of a viscous solid. Given a wire of the solid of length l and radius R. Let its upper end be fixed and the lower end be attached to a heavy bob whose moment of inertia for the given conditions is K. Then the equation of motion is (slow oscillation premised)

 $D - K \frac{d^2 \theta_t}{dt^2} = \frac{\pi R^4}{2l} \left\{ \mu \theta_t - \int_0^\infty \psi(\omega) \theta_{t-\omega} d\omega \right\},\,$ 

where D is the moment of the applied couple, \( \mu \) Lamy's

constant, and  $\psi$  some function of  $\omega$ .

Replying to Meyer's critique that a theory of this kind is at variance with the present state of knowledge in atomistics, Boltzmann ‡ disclaims all present purpose to connect his theory with definite physical hypotheses. He points out, however, that the assumed dependence of the existing states of strain on the foregoing deformations is easily justified when the simultaneous changes of molecular configuration are taken into account. For it is not necessary to suppose that the elastic forces, as such, have any dependence on preexisting stress. The changes of configurations in question are closely similar to Maxwell's, so that in this respect Boltzmann's theory may be looked upon as one form of mathematical development of Maxwell's physical hypothesis. I may add that Boltzmann himself tested his theory with data of Kohlrausch, Neesen, and Streintz. A special series of experiments subsequently undertaken by Kohlrausch § give addi-

<sup>\*</sup> Boltzmann, Pogg. Ann. Ergänzb. vii. p. 624, 1876.

<sup>†</sup> Kohlrausch, Pogg. Ann. clx. p. 227, 1877. ‡ Boltzmann, Wied. Ann. v. p. 430, 1878. § Kohlrausch, Pogg. Ann. clx. p. 225, 1877.

tional strength to Boltzmann's deductions. The theory,

however, does not predict permanent set.

A theory similar to Boltzmann's, but of an atomistic kind, is due to Neesen \*. It also assumes the occurrence of solid viscosity. Neesen distinguishes the forces producing and retarding motion and the final purely elastic forces which obtain after motion has subsided. Neesen practically postulates a change of the constants of elasticity. Warburg t objects to Neesen's deductions because they contain no reference to the form of the molecule. Meyer fails to find in it definite causal relations to the observed viscous motion.

Braun's researcht, though largely experimental in character, deserves mention here, because of special light which it throws on the superposition of different viscous deformations. Excepting glass, he finds that these molecular motions do not take place independently of each other. He concludes that elastic and viscous deformation owe their occurrence to forces of different origin, and he refers the viscous deformations to the partial molecular rotation postulated by Weber and by Kohlrausch.

Warburg &, following out the suggestions contained in Braun's results, formulates a new theory in which viscosity is the result of partial rotations of finite molecules of a form

other than spherical.

Nissen's || theory is unique. He considers the æther in the space surrounding the body, in its relations to the æther within the intermolecular spaces of the body; and he bases his theory of viscosity on the conditions under which the external æther enters the said intermolecular spaces, when the body is deformed by stress. He thus obtains both a time and a thermal effect. In many respects this curious theory seems to me to anticipate Osborne Reynolds's ¶ in recognizing the importance of the "dilatancy" of a granular medium.

3. Maxwell's \*\* theory would require more extended comment; but the terms in which his views are expressed are so precise that it is impossible to abbreviate them. The reference must, therefore, here suffice; cf. §§ 9, 14. Aside from the remarks of the next paragraph, the ideas underlying Maxwell's

\* Neesen, Pogg. Ann. clvii. p. 579, 1876. † Warburg, Wied. Ann. iv. p. 233, 1878.

<sup>‡</sup> Braun, Pogg. Ann. clix. p. 337, 1876; cf. Kohlrausch, Pogg. Ann. clx. p. 227, 1877. § Warburg, Wied. Ann. iv. p. 232, 1878.

Nissen, Inaug. Dissert., Bonn, 1880. (Not accessible in Washington.) ¶ Reynolds, Rep. Brit. Assoc. 1885, p. 896; Phil. Mag. [5] xx. p. 469, 1885.

Maxwell, l. c. p. 311.

theory have been given by many others, indeed by almost all the chief writers on solid viscosity; but Maxwell carries them

through consistently to a complete theory.

I have stated that Maxwell's theory of viscosity is the analogon of Clausius's theory of electrolysis. Where the latter uses "Theilmoleküle" and electromotive forces to effect chemical decomposition, Maxwell has unstable configurations and stress available to produce permanent deformation. Clausius's case the number of decomposable molecules (i. e. unstable configurations as regards the action of electromotive force) in any given case of actual electrolysis is practically This corresponds to Maxwell's viscous fluid, hard or In a viscous solid molecular configurations are present in all degrees of stability, with a sufficient preponderance of stable configurations to constitute a solid framework. The relative number of unstable configurations varies with the viscosity of the material. If, therefore, I conceive the case of an electrolyte exhausting itself in respect to electrical conductivity by the chemical decomposition induced by current, until conduction cease, I have the analogon of a solid which is reaching the limit of viscous deformation.

From this analogy it follows that a solid (?) electrolyte is necessarily viscous; whereas a viscous solid is only an electrolyte when the configurations break up into parts oppositely charged. Again, a viscous solid (?) is probably more viscous when undergoing electrolytic decomposition than when no current passes through it. Experiments to the same effect can, however, be made with greater facility if the solid operated on is such that special instability of molecular configuration can be superinduced by heat instead of electrical action. Such a solid is hard steel, in which, in addition to the ordinary thermal instability, what may be called a carburation instability of molecular configuration asserts itself, even at mean atmospheric temperatures. Inasmuch, therefore, as the gist of Maxwell's theory is stability of molecular configuration, it follows that the evidence which can be derived with reference to it from hard steel must be unique in character: for, despite the extreme hardness and rigidity of tempered steel, instability of molecular configuration demonstrably exists \* and is distributed uniformly throughout the metal; moreover the number of unstable molecular groups can be made to vary over an enormous range at pleasure.

4. Perhaps the experiments already made on the viscosity

<sup>\*</sup> Barus and Strouhal, American Journ. [3] xxxii. p. 276, 1886.

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of steel\* are a sufficient guarantee for the remarks of this paper; but as the above paragraphs clearly show that data tending to throw light on the ultimate nature of viscosity are urgently called for, I shall add some further experimental results. To obtain these I made use of a perfected form of the differential apparatus described elsewhere†.

For several purposes touched upon in the course of the present work it is necessary to indicate the theory of the said differential apparatus more fully than was done in the earlier

paper. This I will briefly do here.

Given a continuous straight steel wire, of length L, to which a convenient rate of twist,  $\tau$ , has been imparted. Consider two right sections whose distance apart is the unit of length, and let  $2\phi$  be the amount of viscous angular motion of the first relative to the second during the given small time t and for the fixed rate of twist  $\tau$ . To fix the ideas, let the wire be adjusted vertically, and provided with an index to register angular motion at a distance l' above the lower end. Then will the motion at the index due to the viscous detorsion of two sections whose position is x, and whose distance apart is dx (x>l'), during the time t be

$$d\psi = \frac{l'}{x}\phi dx.$$

For at every section the viscous motion is such that if the contiguous parts immediately below the section slide in a given direction, the parts immediately above it slide in equal amount in the opposite direction. Again, of the two equal and opposite viscous motions which take place at any section, only the

motion of the part nearest the index will influence it.

This premised, suppose, furthermore, that the parts of the wire below the index, the parts whose position is 0 to l', be kept at a given constant temperature and be of the same temper throughout. Let those parts also of the wire above the index be of the same or any other uniform temper, but let them be heated to different constant temperatures. Thus let the viscous detorsion between x=0 and x=l' be typified by  $\phi'$ ; between x=l' and  $x=\beta$  by  $\phi_3$ ; between  $x=\beta$  and  $x=\alpha$  by  $\phi$ ; between  $x=\alpha$  and x=L by  $\phi_1$ : in which the difference of  $\phi_1$ ,  $\phi$ ,  $\phi_3$  are evoked by differences of temperature of the parts of the wire to which these data refer, whereas  $\phi'$  may differ from all these by an increment of temper of any value, as well as of temperature. Then the influence of the viscous detorsion in each of

Amer. Journ. [3] xxxii. p. 444, 1886; ibid. xxxiii. p. 20, 1887.
 Amer. Journ. [3] xxxiv. p. 2, 1887.

the parts in question, on the index whose position is x=l', will be

$$l'\phi_1\int_a^L \frac{dx}{x}, \quad l'\phi\int_\beta^\alpha \frac{dx}{x}, \quad l'\phi_3\int_{l'}^\beta \frac{dx}{x}, \quad l\phi'\int_0^l \frac{dx}{L-x};$$

where l = L - l'.

Hence the motion of the index,  $\psi$ , is

$$\psi = l \left( \phi_1 \ln \frac{L}{\alpha} + \phi \ln \frac{\alpha}{\beta} + \phi_3 \ln \frac{\beta}{l'} \right) - l \phi' \ln \frac{L}{l}.$$

Now, if the experiment is so conducted that  $\phi_1 = \phi_3 = \phi'$  and  $l = l' = \frac{1}{2}L$ , which implies uniformity of temper throughout the wire from 0 to L, then

$$\psi = l(\phi - \phi') \ln \frac{a}{\beta},$$

which suggests the most convenient method of experiment. If it is possible to heat the upper wire uniformly throughout its length, this equation takes the simpler form

$$\psi = l(\phi - \phi') \ln 2$$
.

If  $\phi'$  is negligible relatively to  $\phi$ , this method leads to absolute results.

There is another case which facilitates experiment. Let  $\phi_1 = \phi_3$ ,  $\phi' = 0$ , l = l'. Then

$$\psi = l\phi_1 \ln 2 + l(\phi - \phi_1) \ln \frac{\alpha}{\beta}$$
.

If the behaviour of the wires for  $\phi = \phi_1$  (i. e. for the case in which the upper wire has the uniform temperature corresponding to  $\phi_1$ ) be known, this equation is similar to the preceding. In general and intermediate cases correction members must be investigated.

If a series of detorsions,  $\phi$ , be observed at  $\theta^{\circ}$ , and another series,  $\Phi$ , be observed at  $\Theta^{\circ}$ ; if  $\phi = \phi_0$ ,  $F(\theta)$  and  $\psi = n/2R$ 

(Gauss's method of angular measurement), then

$$\phi_0[F(\Theta)-F(\theta)] = \frac{N-n}{RL \ln 2},$$

where R is the distance between Gauss's mirror and scale in centimetres, and where N and n are the scale-parts (centims.) corresponding to  $\Theta^{\circ}$ ,  $\theta^{\circ}$ , respectively. Hence, whatever be the function F, the distance of the individual curves for  $\Theta^{\circ}$  and  $\theta^{\circ}$  apart varies directly as  $\phi_0$ . This result, though simple enough, has special bearing on certain data below.

5. The following tables exhibit the new results for hard steel. About 20 rods (diameter  $2\rho = .081$  centim.) were examined. Table I., after enumerating the rod ("No.") and stating the temperature at which it was annealed ("An.") from glasshardness, gives the amount of twist  $\tau$  (radians) temporarily imparted per unit of length, and  $2(\phi + \phi')$  the mean amount of viscous detorsion, in radians, per unit of length, observed immediately after the end of the experiment.  $2(\phi + \phi')$  is therefore the mean viscous effect of  $\tau$  stored in the system of

two vertical wires. Hence  $\tau + 2$   $(\phi + \phi') = \frac{2\pi}{L}$ . Furthermore  $\theta'$  is the temperature of the lower wire,  $\theta$  that of the upper wire, and  $\frac{\phi - \phi'}{\tau}$  (radians) is the amount of viscous

angular detorsion, as observed at the index between the wires, at the time specified, per unit of  $\tau$ . Regarding this differential quantity, which is the chief datum of these tables, it is merely necessary to call to mind that  $2\phi$  is the amount of viscous detorsion, in radians, per unit of length of the upper wire, for the rate of twist  $\tau$ ; and  $2\phi'$  has the same signification relatively to the lower (normal) wire. The reference to unit  $\tau$  is a convenience permissible when  $\tau$ , as in the present work, has nearly the same value throughout \*.

The normal wire, No. 1, with which all the other steel wires are compared, is annealed from hardness at 450°, and has been twisted back and forth till viscosity is practically unchanged by further twisting within the same limits. It is, therefore, in a state of extreme viscosity, and, at the same time, less liable to permanent set than a soft steel wire. Its dimensions are l'=30 centim,  $\rho'=0405$  centim., so that l=l'. The wire of unknown viscosity is examined at 20° (nearly), and immediately after at 100°. Two experiments are made at each temperature with  $\tau$  alternately positive and negative. When  $\tau$  and  $(\phi-\phi')/\tau$  have like signs (the usual case), the lower wire (No. 1) has the greater viscosity. In case of  $\theta=100^\circ$ , only a part of the upper wire,  $\alpha=\alpha-\beta$ , could be heated; the remainder  $\beta$  being kept at the lower temperature  $\theta'$ . Time is conveniently given in minutes.

<sup>\*</sup> In how far such reductions are generally permissible, cf. Weidmann, Wied. Ann. xxix. pp. 220, 222, 1886.

Table I.—Viscous Detorsions of Hard Steel. l=30 cm.  $\rho=0.0405$  cm. a=28.5 cm.  $\beta=31.5$  cm.

No. An.	$2(\phi+\phi').$	θ'. θ.	Time.	$\frac{\phi - \phi'}{\tau} \times 10^3$ .	No.	$2(\phi+\phi').$	θ'. θ.	Time.	$\frac{\phi - \phi'}{\tau} \times 10^3$ .
<b>2.</b> 450°.	Radians1045	° C. 20 20	Minutes. 3 17 50 60	Radians. +0·00 0·04 0·07 0·09	<b>2.</b> 450°.	Radians, 1027	° C. 100 20	Minutes.  2 6 18 29 45 58	Radians0.00 -1.35 -2.89 -3.66 4.53 -5.10
	+·1027 +·0020	20 20	1 8 28 52	-0.00 09 18 18		+·1027 +·0020	100 20	2 20 33 47	+0·00 2·51 3·76 4·72
<b>3.</b> 450°.	-·1033 -·0014	20 20	2 6 19 28 44	+0·00 ·25 ·49 ·63 ·71	<b>3.</b> 450°.	-·1027 -·0020	100 20	2 11 20 34 48	0·00 -1·30 -1·78 -2·22 -2·89
	+·1030 +·0017	20 20	2 8 20 30	0·00 ·04 ·04 ·04		+·1027 +·0020	100 20	2 10 18 24	+0.00 4.58 6.84 8.09
<b>4.</b> 360°.	-·1033 -·0014	22 22	2 17 42 54	-0.00 27 35 35	<b>4.</b> 360°.	- 1007 - 0041	100 22	3 15 28 46	-0.00 -2.56 -3.64 -4.48
	+·1007 +·0041	22 22	1 33 44 64	+0·00 2·13 2·33 2·56		+ 0049	100 22	2 12 22 37 49	+ 0·00 7·83 11·21 14·49 16·28
<b>5.</b> 360°.	-·1027 -·0020	23 23	2 15 21 34	-0.00 27 36 40	<b>5.</b> 360°.	<b>-</b> ·1019 ·0029	100 23	3 22 32	-0.00 -3.30 -4.32
	+ 1021 + 0026	23 23	2 12 19 27	+0·00 ·36 ·42 ·45		+ 1015 + 0032	100 23	2 7 20 27	+0·00 3·12 5·94 6·97

Table I. (continued).

No. An.	$\tau$ . $2(\phi + \phi')$ .	θ'. θ.	Time.	$\frac{\phi - \phi'}{\tau} \times 10^3$ .	No. An.	$2(\phi-\phi').$	θ'. θ.	Time.	$\left  \frac{\phi - \phi'}{r} \times 10^3 \right $
<b>6.</b> 190°.	Radians. 1035	° C. 19 19	Minutes. 2 5 17 35	Radians0.00184026	<b>6.</b> 190°.	<b>-</b> ·1023	° C. 100 19	Minutes. 1 4 12 20	Radians. - 0.00 - 5.42 -11.79 -15.28
						- 0024		29 36	$-19.05 \\ -19.63$
	+·1035 +·0012	19 19	2 19 31	-09 -00 +0.00		+·1003 • •••0044	100	1 5 10 15 20 26 32 38	$\begin{array}{c} +\ 0.00 \\ 12.02 \\ 19.53 \\ 24.96 \\ 28.71 \\ 32.56 \\ 35.42 \\ 38.02 \end{array}$
<b>7.</b> 190°.	-·1027 -·0020	20 20	2 8 18	-0.00 -0.93 -1.48	<b>7.</b> 190°.	-·1007 -·0041	100 20	1 3 8 19 33 40	- 0.00 - 5.70 -16.33 -28.63 -36.79 -39.64
	+.0038	20 20	1 9 20 30 50	+0.00 1.69 2.56 3.01 3.74		+·1003 +·0044	100 20	2 9 16 26 40	+ 0.00 15.89 23.58 30.39 36.40
8. 190°.	- · 1035 - · 0012	20 20	2 12 19 27	-0.00 35 54 54	<b>8.</b> 190°.	- · 1007 - · 0041	100	3 11 20 32 55	$\begin{array}{r} -0.00 \\ -13.27 \\ -21.34 \\ -27.45 \\ -35.12 \end{array}$
	+·1030 +·0017	20 20	2 9 17 33 44	+0.00 0.63 1.03 1.43 1.66		+·0995 +·0052	100	2 11 22 28 41	+ 0.00 25.08 39.11 43.09 50.86

Table I. (continued).

No. An.	$7$ $2(\phi+\phi')$ .	θ'. θ.	Time.	$\frac{\phi - \phi'}{\tau} \times 10^3$ .	No. An.	$\tau$ $2(\phi-\phi')$ .	θ'. θ.	Time.	$\frac{\phi - \phi'}{\tau} \times 10^3$
<b>9.</b> 100°.	Radians 1033 0014	° C. 19 19	Minutes. 2 8 27	Radians. -0.00 -0.79 -2.14	<b>9.</b> 100°.	Radians.	° C. 100 19	Minutes. 2 5 8	Radians 0.00 -25.74 -39.60
	+·1023 +·0023	19 19	3 10 31 42	+0·00 1·49 3·37 3·97		A	 ccident.		
<b>10.</b> 100°.	- 1041 - 0006	20 20	1 12 25 38	-0.00 -1.33 *-1.94 -2.39	<b>10.</b> 100°.	-·0974 -·0073	100 20	1 3 7 16 19 21	- 0.00 -29.97 -47.54 -82.69 -91.64 -96.51
	+·1023 +·0023	20 20	2 21 45	+0·00 2·52 3·60	A	+·0968 +·0078	100 20	2 5 8 12 18 22 25 32 35 42	+ 0·00 22·18 35·89 48·97 63·17 70·81 76·16 87·40 90·05 99·65
<b>11.</b> 100°.	-·1033 -·0014	21 21	1 8 32 48	-0.00 -0.67 -1.16 -1.29	<b>11.</b> 100°.	-·1007 -·0041	100 20	2 5 10 16 22 26	- 0·00 -12·59 -23·80 -32·45 -38·95 -42·69
	+ 1027	21 21	2 12 26 37 50	+0·00 1·71 2·65 3·14 3·57		+.0081	100 20	3 5 16 23 31 37 45	+ 0.00 8.51 45.41 59.98 73.30 81.72 91.75

Table I. (continued).

	· · · · · · · · · · · · · · · · · · ·	1			)	1	1	)	1
No. An.	$2(\phi+\phi')$ .	$\theta'$ . $\theta$ .	Time.	$\frac{\phi - \phi'}{\tau} \times 10^3.$	No. An.	$\tau$ . $2(\phi + \phi')$ .	θ'. θ.	Time.	$\frac{\phi - \phi'}{\tau} \times 10$ .
12. 25°.	Radians. + 1007	° C. 22 22	Minutes.  2 5 11 29	Radians. + 0.00 3.30 6.14 10.07	<b>14.</b> 25°.	Radians.	° C. 20 20	Minutes. 2 10 21 31	Radians 0.00 - 5.78 - 8.63 - 10.19
	+.0041		36	11 07		0044		42	-11.48
	-·0993 -·0053	22 22	$\begin{array}{c} 2 \\ 13 \\ 20 \\ 25 \end{array}$	$ \begin{array}{rrr}  & -0.00 \\  & -7.41 \\  & -9.16 \\  & -10.26 \end{array} $		+.0989	20 20	2 7 14 18	0.00 4.19 6.89 7.96
	_ 0000		20	-10 20	·	+.0057		23	8.95
13. 25°.	1007	20 20	$\begin{array}{c c} 3 \\ 12 \\ 22 \end{array}$	-0.00 -3.52 -5.26		<b>-</b> ·1021	20 20	5 15 37	- 0.00 - 1.99 - 4.11
	0041		36	-6.87				57 63	- 5·18 - 5·60
	+.1001	20	2	+0.00		0026		82	- 6.38
		20	6 14 26 31	2·90 5·66 7·92 8·61		+·1019 +·0029	20 20	1 111	+ 0.00
	+.0047		41	9.62	- W	1.1041	93	0	1 0 00
	1019	20 20	4 9 17	0·00 1·09 2·26	17. 100°.	+ 1041	22 22	12 12 22 34	+ 0.00 $1.50$ $2.21$ $2.74$
			23 36 45	2·90 3·98		1033	22	1	- 0.00
	- 0029		59	4·53 5·43		<b>-</b> ∙0014	22	15 28 40	$\begin{array}{c c} - 2.41 \\ - 3.21 \\ - 3.75 \end{array}$
						+.1038	22 22	2 9	+ 0.00 1.15
						+.0009		19 27	1·91 2·26

The following Table II. is interpolated from the preceding, and contains mean values of  $(\phi - \phi')/\tau$ , as derived from the two twists  $\tau$ , alternately positive and negative. The justification of this mode of obtaining data for a chart is indicated in § 9. Besides these data, Table II. contains the number and temper

("An."), and the electrical constant \* (specific resistance  $s_0$ , microhms, c.c., 0° C.), as well as the differences  $s_0-s'_0$  and  $s_{100}-s'_{20}$ , in which the subscripts are the temperatures at which s is taken, and s' is the constant of the normal rod No. 1. Hence these electrical differences correspond to  $(\phi-\phi')/\tau$ , when  $\theta=0^\circ$  C. and  $\theta=100^\circ$  C. respectively. For No. 1, therefore,  $s'_0=13.6$ ;  $s'_0-s_0=0$  and  $\phi-\phi'/\tau=0$ .

The values  $(\phi - \phi')/\tau$  are in the same horizontal row with

the temperature  $\theta$  to which they belong.

Table II.—Values of  $\frac{\phi - \phi'}{\tau} \times 10^3$  at different consecutive times.

No.	$s_0 - s'_{0}$ , $s_{100} - s'_{20}$ .		:		T	ime =			
s <sub>0</sub> .	s <sub>100</sub> —s' <sub>20</sub> .	θ.	2m.	5m.	10m.	20m.	30m.	40m.	50,m.
$ \begin{array}{c} \circ \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $	0·8 5·9 0·6 5·6	20 100 20 100	+0.00 +0.00 +0.00 -0.00	- ·04 + ·82 - ·09 +1·69	-·07 1·65 -·18 2·90	-·10 2·76 -·28 4·48	-·12 3·63 -·34 5·75	-·14 4·26 -·38	-·15 4·84 -·40
$ \begin{array}{c} \text{VOI} \\ 0.028 \\ 19.0 \\ 5 \\ 20.1 \end{array} $	0·4 5·5 1·5 6·5	$   \begin{array}{c}     22 \\     100 \\     23 \\     100   \end{array} $	0.00 0.00 0.00 0.00	21 2·32 11 1·65	·50 4·70 ·25 2·90	*82 7:05 *37 4:60	1·00 8·70 •43 5·88	1·09 9·80	1·17 10·80
$\begin{array}{c} \text{uV} \\ \begin{array}{c} 6 \\ 28.8 \\ 7 \\ 30.9 \\ 8 \\ 31.3 \end{array} \end{array}$	10·2 15·8 12·3 17·7 12·7 17·8	19 100 20 100 20 100	0.00 0.00 0.00 0.00	·09 ·4·40 ·67 7·50 ·21 9·00	·18 11·00 1·27 16·30 ·49 19·00	·23 18·70 1·90 26·50 ·83 30·20	•23 23·30 32·20 •98 36·70	26·40 36·50 41·30	
$ \overset{\circ}{\mathbf{H}} \left( \begin{array}{c} 9 \\ 37.2 \\ 10 \\ 34.2 \\ 11 \\ 33.5 \end{array} \right) $	18·6 24·2 15·6 21·0 14·9 20·5	19 100 20 100 21 100	0.00 0.00 0.00 0.00	·44 25·70 ·63 20·50 ·47 13·00	·98 48·50 1·25 41·00 1·00 28·50	1·74 2·00 69·50 1·57 48·00	2·26 2·48 1·90 61·50	2·84 2·14	<b>2</b> ·33
$\begin{array}{c} \begin{array}{c} 12 \\ 39 \cdot 2 \\ 13 \\ 37 \cdot 0 \\ 14 \\ 40 \cdot 6 \end{array} \end{array}$	20·8 18·4 22·1	20 20 20	0.00	3·50 1·67 3·10	6·15 3·29 5·80	8·83 5·15 8·50	10·75 6·35 10·15	11:46	

<sup>7.</sup> Before proceeding to a discussion of the results in Tables I. and II., I will insert a few introductory data which

<sup>\*</sup> For definition of thermo-electric hardness see Bull. U.S. G. S. no. 14, p. 65 (1885).  $s_0-s'_0$  and  $s_{20}-s'_{20}$  need not be distinguished in the above.

hold for pure platinum. The plan of comparison and tabulation is the same as that explained for steel, in the remarks preceding Table I.  $\tau$  here is small, and  $2(\phi + \phi')$  large relatively to the data in Table I., because soft platinum is much more liable to assume permanent set than annealed steel. Moreover  $\tau$  is impressed negatively throughout; the changes of sign of  $(\phi - \phi')/\tau$  are explained in the text below the table, and it is to this text that the letters  $a, b, \ldots f$ , refer.

Table III.—Viscous Detorsions of Platinum.  $\theta = \theta'$ .

	$r$ $2(\phi+\phi')$ .	Remarks.	Time.	$\frac{\phi-\phi'}{\tau}\times 10^3$ .
em. l=26·2 ρ=·0215	<b>-</b> ∙0867	a	m. 2 9 15	- 0·00 - 3·31 - 4·42
	0344		27 33	- 5.65 - 5.89
	0652	ь	$\frac{2}{17}$	- 0.00
	0556		$\begin{array}{c} 17 \\ 44 \end{array}$	- 3·59 - 4·20
	- 0443	С	$1 \\ 4 \\ 14 \\ 28$	+0.00 $20.60$ $46.80$ $61.90$
	- 0766		44	71.90
	0436	d	$\begin{array}{c} 2 \\ 7 \\ 17 \\ 25 \\ 43 \end{array}$	$ \begin{array}{r} -0.00 \\ -22.20 \\ -41.40 \\ -50.20 \end{array} $
	0773		54 54	$-61.40 \\ -65.80$
	-0383	e	3 7 26 47	$\begin{array}{r} + 0.00 \\ 5.56 \\ 19.60 \\ 27.80 \end{array}$
	0826		55	30.00
l=26·5 ρ=·0212	0396	f	3 8 13 29 37	$ \begin{array}{r} -0.00 \\ -10.90 \\ -17.50 \\ -29.20 \\ -33.00 \end{array} $
	0813		46	-36.80

The two wires of Table III. were originally identical, so that the apparatus showed  $\phi - \phi' = 0$ . Both wires were then

twisted, but the lower more than the upper. The results under a indicate greater viscosity for the lower, a state of things which is only partially wiped out by annealing at red heat, in air, as indicated under b. I then commenced the experiments proper, by leaving the upper wire untouched and annealing the lower wire at red heat. The results, under c. indicate an enormous difference, the unannealed wire being of greater viscosity. I then left the lower wire untouched and annealed the upper at red heat. The results under d again show an enormous difference, the unannealed wire (now the lower) being of greater viscosity. I then again annealed the lower wire only, obtaining the results under e, corresponding to c; and, finally, again annealed the upper wire only, obtaining the results under f, corresponding to d. The operation of alternate annealing might have been continued very much longer with practically the same results. In each case the freshly annealed wire shows pronounced loss of viscosity, as compared with an otherwise identical wire, slightly twisted beyond the elastic limits.

As compared with the effects of alloying, I found this mechanical result so large as to compel me to abandon my experiments on the viscosity of series of platinum alloys—at least until the mechanical error in question has been interpreted and brought under control. To return to the mechanical phenomenon in question, I may remark that the result of heating a thin wire red hot in air, without precautions for slow cooling, is a strain of dilatation imparted to the wire. Hence molecular stability of a lower order than would obtain if cooling had taken place with extreme slowness. Again, if the dilated wire be twisted even over small arcs of permanent set, the greater number of the more unstable configurations will be mechanically broken up; for the prevailing tendency must be such as to cause these continually to fall into positions of minimum potential energy. Twisting indefinitely repeated

therefore produces marked hardness and elasticity.

When two wires, chemically and physically as nearly identical as possible, are compared, it is conceivable that viscosity will vary with the time elapsed after annealing. Many experiments were made, and showed slight increase of viscosity with the time given to the molecules to subside after annealing in air; but the results\* were insignificant in magnitude, often obscure, and not at all comparable with the

<sup>\*</sup> This proves that in Schröder's paper (Wied. Ann. xxviii. p. 369, 1886) the observed thermal "accommodation" was the result of annealing hard-drawn wire.

data of Table III. It follows that the results of this table are not a direct heat-effect subsidence of accumulated heat agitation.

Again, the sign of the twist,  $\tau$ , in Table III. is the same throughout. It must therefore be asked whether in these experiments an earlier stage of viscous subsidence simply overtakes a later stage. To throw light upon this point it is sufficient to reverse the sign of the twist alternately, without fresh annealing: or to reverse the sign of the twist with each alternate annealing of the upper and lower platinum wire. In such a case a latent strain \* favourable to motion is imparted to the wire not annealed. Experiments which I made in some number showed that, even in this case, the results of Table III. hold good, the character of the motion being diminished in degree, but not in sign.

All these results are such as follow at once from Maxwell's They show that the above viscous effect of twisting is to be referred to the motion of molecules which accompanies it; molecules and atoms are thus placed in new positions and relations to each other; unstable configurations during the course of such motion are therefore continually broken up into configurations of smaller potential energy and greater stability. Hence, finally, the observed increase of viscosity. By reversing the sign of the twist, the original configurations can only be partially restored, at best, even for small permanent set, such as is here in question. Finally the effect of prolonged and repeated twisting is stiffness, because all the molecules have collapsed into configurations of maximum stability, and the intrinsic molecular energy is the potential minimum compatible with the given conditions. In the next paragraph (8) this is shown to better advantage with steel.

8 a. Steel wires were used in our earlier work † free from torsional strain. The hard steel wires of the present paper, employed in other work, may contain twists stored up like permanent magnetism. This produces a kind of unilateral symmetry, so far as torsions are concerned; but it is not otherwise objectionable. In critical cases wires free from lateral torsion are selected.

Turning to Table I., the individual wires enumerated are found to show wide differences of viscous behaviour. In No. 2 the viscous subsidence takes place at nearly the same rate

<sup>\*</sup> Cf. § 8, closing remarks.

<sup>†</sup> B. and S., American Journ. [3] xxxii. p. 448, 1886; *ibid.* xxxiv. p. 4, 1887.

for  $-\tau$  and for  $+\tau$ , both at  $\theta=20^\circ$  and  $\theta=100^\circ$ . In No. 3 the effect of  $-\tau$  and  $+\tau$  is of different magnitude at  $20^\circ$  and enormously more different in magnitude at  $100^\circ$ . In No. 4 the effect of  $+\tau$  following  $-\tau$  is even more phenomenally pronounced, both at  $20^\circ$  and particularly at  $100^\circ$ . In No. 5 the wires nearly identical at  $20^\circ$  show differences at  $100^\circ$ . In No. 6 this is true even in much greater degree, whereas in No. 7 wires differing considerably at  $20^\circ$  show relatively small differences at  $100^\circ$ . And so I might go through the series. The element of vagueness asserts itself throughout, and is almost serious enough to obscure the law. Nor is this wholly due to the latent torsions mentioned at the outset of this paragraph. Nos. 13 and 14 are wires originally free from torsional strain; but the said vagueness also appears in these.

Careful inspection of the tables reveals the law that viscous deformation takes place at numerically greater rates during the even twists than during the odd twists which immediately and respectively precede them. Irrespective of these oscillations, the effect of twisting here, as in § 7, is pronounced

increase of viscosity.

Maxwell's theory accounts for the stated vagueness of behaviour at once. In two samples of a complex substance like steel, the distribution and relations of the unstable molecular configurations will only in very rare instances be physically and chemically identical. The previous paragraph shows that

such identity is rare even in pure homogeneous metal.

The effect of twisting alternately in opposite directions is of such great importance in its bearing on Maxwell's theory that I made further special experiments. From these I select the following typical instance, tabulating it in the way adopted in Table I. The normal No. 1, An. 450°, has been described. No. 18, An. 25°, or glass-hard, is carefully selected free from latent torsion, having experienced no other strain prior to the examinations in Table IV. than that incident to tempering (quenching). There are 12 alternations of twist, indicated by subscripts, and the current time in hours and minutes of each is given. I also give, under m, the time in minutes which refers specially to the duration of each twist. No. 1 being always of greater viscosity,  $\tau$  and  $(\phi-\phi')/\tau$  are alike in sign, by agreement.

Table IV.—Viscous Effect of Twisting alternately in opposite Directions.

Normal wire No. 1. l=30 cm.  $\rho=0.0405$  cm.

Remarks.	τ.	Time.	m.	$\frac{\phi-\phi'}{\tau}\times 10^3$ .	Remarks.	τ.	Time.	m.	$\frac{\phi-\phi'}{\tau}\times 10^3$ .
18 <sub>1</sub> . An. 25°.	<b>-</b> ·102	h m 9 13 15 17 28	0 2 4 15	-0.00 -0.10 -5.90	18 <sub>8</sub> .	+102	h m 12 0 2 4 20	0 2 4 20	+0.00 0.85 3.80
182.	+·102	35 9 37 39 41 52	22 0 2 4 15	$ \begin{array}{c c} -7.30 \\ +0.00 \\ 2.30 \\ 7.50 \end{array} $	189.	102	12 24 26 28 40	0 2 4 16	-0.00 -0.60 -3.45
18 <sub>3</sub> .	<b>-</b> ·102	10 2 4 8 19 25	23 0 2 6 17 23	9·35 -0·00 -2·10 -4·75 -5.70	18 <sub>10</sub> .	+102	12 42 44 46 54 63	0 2 4 12 21	+0.00 0.80 2.55 3.70
184.	+.102	10 28 30 36 41	0 2 8 13 20	-5·70 +0·00 2·95 4·40	18 <sub>11</sub> .	<b>-</b> ·102 <b>+</b> ·102	1 5 7 9 21 1 23 25	$\begin{bmatrix} 0 \\ 2 \\ 4 \\ 16 \\ 0 \\ 0 \end{bmatrix}$	-0.00 -0.65 -2.55
185.	102	10 50 52 59 70	0 2 7 20	5·60 -0·00 -2·30 -3·95		After s	25 27 36 several day	$ \begin{array}{ c c } 2\\4\\13\\ \hline ys:\\ \end{array} $	+0.00 0.70 2.45
186.	+.102	11 11 13 15 25 33	0 2 4 14 22	+0.00 1.10 3.75 4.95	18 <sub>13</sub> .	- 102	9 47 49 51 60	0 2 4 13	-0.00 -0.90 -3.00
187.	102	11 35 37 39 56 57	0 2 4 21 22	-0.00 -0.75 -3.45 -3.55	18,4.	+:102	10 2 4 6 15	0 2 4 13	+0.00 1.00 6.40

Similar experiments made by countertwisting glass-hard wires gave results like this, but on a smaller scale. To compare the results of Table IV. perspicuously, it is sufficient to construct the difference  $\Delta(\phi-\phi')/\tau$ , of the respective values

of  $(\phi - \phi')/\tau$ , at two minutes and four minutes after twist is imparted. These are then to be compared in their dependence on current time. Phenomena of this kind were called viscous "accommodation" by Streintz\*, Kohlrausch†, Wiedemann‡, and others.

Table V.—Viscous "Accommodation" of Glass-hard Steel.

Twist No.	Current time.	$\Delta \frac{\phi - \phi'}{\tau} \times 10^3$ .	Twist No.	Current time.	$\Delta \frac{\phi - \phi'}{\tau} \times 10^3.$
1 2 3 4 5 6	minutes. 0 24 49 75 97 118	$\begin{array}{c} -1.90 \\ +2.30 \\ -1.20 \\ +1.40 \\ -1.00 \\ +1.10 \end{array}$	7 8 9 10 11 12	minutes. 142 167 191 209 232 250	-0.75 +0.85 -0.60 +0.80 -0.65 +0.70

If, as in fig. 2 (p. 204), the numerics of  $\Delta(\phi-\phi')/\tau$  be regarded in their dependence on time, the results are seen to oscillate round a mean line of equilibrium. The ordinates of this mean line decrease with time at a gradually retarded rate until a definite inferior limit is eventually reached. It is curious to note that the largest observed ordinate (time = 0 nearly) is at least three times the limiting ordinate (time =  $\infty$ ). After twelve twists oscillation has considerably subsided, but it has not ceased; in the same degree the viscosity of the

glass-hard steel rod has reached a fixed maximum.

This complicated phenomenon ("accommodation") is at once elucidated by Maxwell's theory. The ordinates of the line around which oscillation takes place are an index of the degree of instability of molecular configuration at the time given by the abscissæ. The oscillations are the result of strain (latent torsion I called it above) imparted to the configurations by the successive twists to which the wire is subjected. Thus, if  $\tau$  be the impressed twist and  $\Delta \tau$  the mean strain left in the configurations at the instant when  $\tau$  is removed, and if n be the original relative number of unstable configurations, and  $\Delta n$  be the number broken up during the period of the strain  $\tau$ ; then (apart from subsidiary considerations) Maxwell's theory analyzes the effects of alternate twisting in accordance with the following scheme:—

\* Pogg. Ann. cliii. p. 406, 1874.

<sup>†</sup> Pogg. Ann. clviii. p. 371, 1876; cf. Schmidt, Wied. Ann. ii. p. 48, 1877.

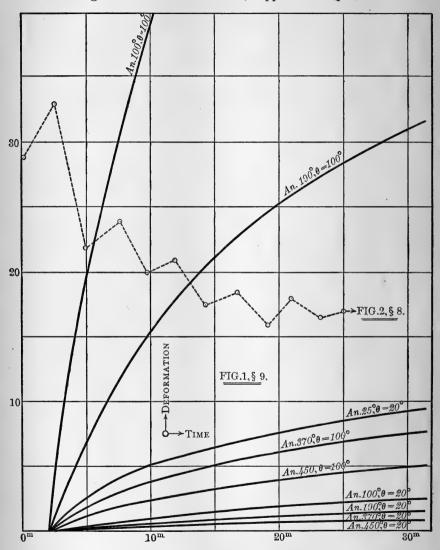
<sup>‡</sup> Wied, Ann. vi. p. 512, 1879.

	Strain.	Molecular stability.	
First twist Second twist. Third twist. Fourth twist. Fifth twist	$-\tau \\ +\tau + \Delta \tau \\ -\tau + \Delta_1 \tau - \Delta' \tau \\ +\tau + \Delta_2 \tau - \Delta_1' \tau + \Delta'' \tau \\ -\tau + \Delta_3 \tau - \Delta_2' \tau + \Delta_1'' \tau - \Delta''' \tau \\ \text{etc.}$	$ \begin{array}{l} +n \\ +n - \Delta n \\ +n - \Delta_1 n - \Delta' n \\ +n - \Delta_2 n - \Delta_1' n - \Delta'' n \\ +n - \Delta_3 n - \Delta_2' n - \Delta_1'' n - \Delta''' n \end{array} $	

The variation which  $\Delta$  undergoes in passing from one twist to the next is indicated by subscripts. Thus  $\Delta \tau, \Delta_1 \tau, \Delta_2 \tau, \ldots$ is probably a decreasing series; whereas  $\Delta n$ ,  $\Delta_1 n$ ,  $\Delta_2 n$ , . . . is an increasing series, because reversal of the sign of the twist must be supposed to reconstruct some of the configurations broken up by the preceding twist. The first part of the scheme indicates that the strain in the 2nd, 4th, 6th, .... twists is necessarily greater than the strain in the immediately preceding 1st, 3rd, 5th . . . . twists respectively; at least at the outset of the experiments. Hence the observed oscillations. Again, the number of unstable configurations must continually decrease, according to the second half of the scheme. Hence the mean line about which the observed viscous deformations oscillate. Finally, experiment shows that the accelerating effect of  $\Delta \tau$  on viscous deformation is greater than the retarding effect of  $-\Delta n$ . After this, however, the accelerating effect of  $\Delta_0 \tau - \Delta_1' \tau + \Delta'' \tau$  and the succeeding  $\tau$ -quantities, is invariably less than the retarding effect of  $-\Delta_2 n - \Delta_1 n - \Delta'' n$  and the succeeding n-quantities respectively. For general purposes the scheme may be simplified. The fact that this phenomenon is reached by Boltzman's mathematical theory is one of its strong features. Of course the period of oscillation is arbitrary.

8b. The second part of Table IV. shows that the viscosity gained in virtue of consecutive alternate twisting of glass-hard steel is permanently gained. Left to itself, the rod does not recuperate, inasmuch as the amount of viscous deformation observed after several days has only increased insignificantly. Mere molecular motion has therefore permanently broken the more unstable carbon configurations. I must waive this singular result here, since it cannot be fully interpreted without electrical research. I will only note, therefore, that the viscous effect of prolonged twisting to and fro in case of glass-hard steel is of the same order of magnitude as the effect of prolonged annealing at 100°. This indicates the importance of the motional effect.

8c. Streintz and Wiedemann's phenomenon "accommodation" admits of representation from a different point of view. Returning to the data of Table IV., suppose the experiments



so conducted that the twelve twists are immediately consecutive. Suppose, furthermore, that m, instead of being reckoned positively onward from the beginning of each of the said

twists, were reckoned alternately positive and negative, conformably with the sign of the deformation  $(\phi - \phi')/\tau$ . In this oscillatory march (time as abscissa), since each deformation (ordinate) now begins where the preceding deformation ceased, a continuous series of open cycles is necessarily generated. The positions of these cycles shift at a gradually retarded rate towards a final, very flat cycle, which for the constant values of time and stress is fixed in position and closed.

Cycles here, closed or not, are expressions of the fact that the "past histories" (in Maxwell's words) of the molecular configurations in the "stress positive" and "stress negative" phase of each cycle are not the same. Shifting is brought about by permanent molecular break-up, the amount of which gradually vanishes. In the ultimate and fixed cycle as many configurations are broken during the "stress positive" as are reconstructed in the "stress negative" phase, though they need not be the same configurations.

These considerations suggest a comparison between "accommodation" and Prof. Ewing's "hysteresis," \* for the purpose of detecting the extent to which like causes are discernible in each phenomenon. Both exhibit a static character. But such a comparison, to be fruitful, calls for direct experiments; for instantaneous values of stress and viscosity must be co-

ordinated.

9. Having thus discussed one phase of the results in Table I., I will pass to Table II., which is a digest of the mean values of Table I., in so far as such a digest can be made. Following the scheme at the end of the preceding paragraph, this comparison should be made after an infinite number of twists have been imparted to each wire. In such a case, however, the original number of unstable configurations has been seriously reduced, so that, apart from the inconvenience of a time-consuming method like this, the original properties of the wire are not clearly present in the results. In wires perfectly free from strain at the outset, the first twist leads to better indications of the viscous quality. As this condition was not always guaranteed for the wires of this paper, I have accepted the mean viscous behaviour during the first and second twists as the best available index for comparison. It is sufficient, at least, for the present purposes. taking the mean for rods of the same nominal temper, I obtain the data from which figure 1 is constructed. Mean viscous deformation  $(\phi - \phi')/\tau$  varying with time is here

<sup>\*</sup> Cf. Phil. Trans. ii. 1885, p. 523; ibid. ii. 1886, p. 361. Prof. Ewing's earlier papers are there mentioned.

graphically shown for the divers tempers, An. 25°, An. 100°, An. 190°, An. 370°, An. 450°. It so happened that the normal is less viscous than the other (An. 450°) rods selected. Hence the negative values of Table II. The axis of abscissa in figure 1 represents Nos. 2 and 3, thus avoiding negative values. Regarding the data for  $\theta = 20^{\circ}$ , it is to be noted that An. 25° are new wires, whereas An. 100° to An. 450° have undergone twisting in earlier work. Hence the experiment exaggerates the size of the interval slightly. The same irregularity affects the distribution of the other degrees of

temper An. 100° to An. 450°.

Returning to Table II., it is clear, inasmuch as viscous deformations are measured differentially, that  $(\phi - \phi')/\tau$  and  $s_0 - s_0'$  are to be compared. It appears that these quantities increase and decrease together. This is more easily discernible when rods free from strain are compared\*. The exceptions of Table II. are due to the fact that latent strains influence  $(\phi - \phi')/\tau$  to a relatively much greater extent than  $s_0 - s_0'$ . Again, if  $s_{100} - s_{20}'$  and  $(\phi - \phi')/\tau$  be compared at 100°, Table II. shows that in this case also the two quantities increase and decrease together. Indeed the data for 100° are the more uniform, a result due to the fact that at 100° much of the latent torsion is made to vanish because of the annealing effect of 100°. Data of even greater uniformity, cæt. par., are to be looked for at higher temperature.

If a comparison is made between the mean rates at which viscous deformation and resistance increase together with temper, at 20°  $((\phi-\phi')/\tau$  and  $s_0-s_0')$  and at  $100^{\circ}$   $((\phi-\phi')/\tau)$ and  $s_{100} - s_{20}$ ), it is seen that the mean rate of increase of  $(\phi - \phi')/\tau$  relatively to s - s' is about ten times as great at 100° as at 20°. This is the phenomenon in virtue of which the viscous behaviour of steel, regarded as a test of Maxwell's theory, is almost crucially important. I shall endeavour to

explain it.

10. Dr. Strouhal and I defined the glass-hard state of steel as the stage of temper which undergoes incipient annealing at mean atmospheric temperature. Inasmuch, therefore, as annealing is demonstrably accompanied by chemical decomposition§, even at temperatures slightly above mean atmospheric, it is clear that the molecular configuration of glass-

<sup>\*</sup> B. and S., Am. Journal [3] xxxiii. pp. 26, 27, 1887.
† The words of Maxwell (l.c.) are:—"... but if, on account of rise of temperature... the breaking up of the less stable groups is facilitated, the more stable groups may again assert their sway, and tend to restore the body to the shape it had before deformation."—Maxwell, l.c.

<sup>‡</sup> Wied. Ann. xi. pp. 962, 963, 1880. § B. and S., Am. Journ. [3] xxxii. p. 276, 1886.

hard steel is always in a state of incipient change. A part, though not the whole, of this change must be of a permanent kind; and I wish to keep in mind that at the temperature of incipient annealing the heat-motion is such that broken con-

figurations are sometimes reconstructed.

Inasmuch, therefore, as glass-hard steel contains a greater number of unstable configurations than any other state of temper at the same temperature, it follows from Maxwell's theory that glass-hard steel, despite extreme hardness, must be the least viscous member of the whole group of tempered and soft steels. This strikingly anomalous prediction of the theory is verified both by the results in Table II. and in figure 1, as well as in earlier work \* in a way so pronounced

as be irrefragable.

If glass-hard steel is annealed at 100°, the greater number of the unstable configurations are broken up in virtue of the increased molecular vibration at the higher temperature. cold rod, after annealing, will show increased viscosity in proportion as the number of unstable configurations has been decreased. Experiment proves this in a strikingly conclusive way: the increase of viscosity thus produced is marked, being nearly half the difference between the soft and hard states of steel. This, too, is an observation favourable to Maxwell's theory; for if there be configurations with an inherent tendency to collapse at ordinary temperatures, it is clear that but a small fraction of them will survive the application of 100°. Moreover, the configurations broken up cannot be reconstructed without the expenditure of fresh energy (quenching). Since no such energy is ordinarily available, the viscous properties of the annealed rod are of a permanent kind.

Again, if glass-hard steel (or steel annealed at 100°) be softened by annealing at 200°, a greater number of unstable groups will be broken up than in the foregoing case. The viscosity of the cold rod must be considerably greater than that of the harder rod. Experiment proves the viscous increase to be about two thirds of the whole viscous difference between hard and soft steel. Analysis gives definite evidence of the occurrence of decomposition; and inasmuch as the unstable groups are permanently broken, the annealed rod shows determinate viscous properties.

If glass-hard steel be annealed at 300°, 400°, 500°, &c., effects of the same nature as those just discussed, but differing from them in the degree of thorough removal of the unstable

molecular configurations, will result.

<sup>\*</sup> Am. Journ. xxxiii. pp. 25, 26, 1887.

The phenomenon considered as a whole must be continuous. both as regards temperature and time. In proportion as temperature is higher, however, Maxwell's theory predicts that the effect of the same increment of the temperature of annealing will produce increments of viscosity successively diminishing at a very rapid rate. Supposing molecular configurations originally present in all states of instability, it follows at once that the groups which retain this quality after annealing must very soon vanish when the temperature of annealing is increased. The data prove this in a convincing Rods annealed at 300°, 400°, 500°, . . . 1000°, show about the same viscous behaviour (relatively speaking), notwithstanding the fact that chemical analysis proves that the decomposition incident to the successive application of these temperatures on glass-hard steel continues steadily to increase\*. Indeed the chemical decomposition above 300° is more marked than below 300°; yet its bearing on Maxwell's theory is now without interest because in none of the high annealed rods do configurations unstable at mean atmospheric temperatures survive after annealing.

11. Having analyzed the phenomena at mean atmospheric temperature, I come next to consider the conditions of mean relative viscosity of steel at 100°. The glass-hard state must here be withdrawn, for consideration in § 13; because such a rod would undergo annealing during the viscous measurements

at 100°.

Hard steel annealed at 100° bears the same relation to 100° that glass-hard steel does to mean atmospheric temperature. Hence the reasoning of the preceding paragraph, mut. mut., applies at once. It is merely necessary to bear in mind that 100° is now the temperature of incipient annealing, and that therefore the temperatures which produce corresponding viscous effects are proportionately higher. Rods An. 200° now occupy about the same relative position that rods An. 100° did in § 9; An. 300° the same relative position as An. 200° in § 9; &c. Moreover, for equal increments of the temperature of annealing, the increment of viscosity shown by the rod at 100° diminishes rapidly as temperature increases; &c.

In one respect the present results differ from the above. The phenomena are here spread out over a scale (roughly estimated) about ten times larger. This means, following Maxwell's theory, that at 100° the number of unstable molecular configurations is relatively much larger than at mean atmospheric

<sup>\*</sup> Am. Journal, xxxii. pp. 277, 282, 1886.

temperature. The reasons for this phenomenon, though not far to seek, are exceedingly significant. In hard steel two causes of molecular instability here produce superposed effects. The first is the chemical or carburation instability already discussed; the second cause is purely thermal. Cf. § 17.

The explanation of the diagram for 100° (fig. 1) is now clear. Viscous deformation is marked in all the rods examined from An. 500° to An. 100°; but the deformability increases at a rapid pace in proportion as we pass from softer to harder steel, because in such a march the carburation instability superimposed upon the thermal instability increases rapidly. Molecular configurations on the verge of instability are encountered in continually increasing numbers.

12. The line of argument followed out for 100° applies, mut. mut., at 200°. Results of this kind I published elsewhere \*. The character of the evidence bearing on all the points in question is here even more pronounced and conclusive. Steel An. 200° is in a state of incipient annealing at 200°. Thermal and carburation instabilities of high degree being encountered, the superimposed effects are correspondingly large.

Finally, above 300° the molecular instability is largely thermal. The behaviour of hard steel, therefore, approaches that of other metals more nearly. The effect of the carburation instability ceases to predominate, and finally vanishes altogether in proportion as the march is made from lower to higher temperatures of annealing.

13. I have finally to touch upon the series of phenomena in which pronounced annealing occurs simultaneously with pronounced external viscous deformation. If, for instance, a glass-hard rod is twisted and then suddenly heated to 100°, the rod is both annealed and suffers deformation in virtue of the applied twist at the given temperature. Conformably with the excessively greater amount of molecular instability which characterizes these experiments, the observed viscous deformation must be proportionately large. This prediction of Maxwell's theory is fully verified by experiment. In the case of the twisted rod postulated, the motion of the image across the field of the telescope is so rapid that Gauss's method of angular measurement is no longer satisfactorily available. I may say, without exaggeration, that during the small interval of time within which appreciable annealing occurs, a glass-hard steel rod suddenly heated to 300° is almost a viscous

fluid. I have shown \* that if a glass-hard and a soft rod (cat. par.) be identically twisted and heated to 350°, the former will have lost the whole of its strain, whereas in the

soft rod only about one third will have vanished.

14. Viscosity in the above pages has been considered apart from the stress (intensity) under which the viscous deformation takes place. This is apt to lead to confusion, unless the stressintensity, relative to which the constants of viscosity are defined, be clearly kept in mind; or unless the term viscosity be applied to solids in the restricted sense of "elastische Nachwirkung." Thus, if a glass-hard and a soft steel rod be subjected alike and at ordinary temperatures to torsional stress of continually increasing magnitude, a stress-value will be reached for which the viscosity of the hard rod will be equal to, and eventually overtake the viscosity of the soft rod. I was able to exhibit this phenomenon in even a more striking way at 190°; finding that for rates of twist less than  $\tau=3^{\circ}$ , the steel rod (radius=0.041 cm.) is much less viscous and, as regards viscosity, much more susceptible to the influence of temperature in proportion as it is permanently harder  $\dagger$ ; whereas for rates of twist greater than  $\tau = 6^{\circ}$ , steel, cat. par., is less viscous and more susceptible to temperature in proportion as it is softer.

Here I may profitably insert certain considerations postulated in an earlier paper 1:—Suppose stress to be so distributed in a solid that its application at any interface is nowhere sufficient to produce rupture. Then that property of a solid in virtue of which it resists very small forces (zero-forces) acting through very great intervals of time (\infty -times) may be termed the viscosity of the solid. That property in virtue of which it resists the action of very large forces (∞ -forces relatively) acting through zero-time may be termed the hardness of the solid. Since the application of forces in such a way as accurately to meet either of these cases is rare, we have, in most practical instances, mixtures of viscous resistances and of hardness to encounter. We may reasonably conceive that in the case of viscous motion the molecules slide into each other or even partially through each other per interchange of atoms, so that the molecular configuration is being continually reconstructed; that in the other case (hardness) the molecules are urged over and across each other, and that therefore the intensity of cohesion is in this case more or less thoroughly

<sup>\*</sup> Amer. Journ.[3]xxxiv. pp. 4, 5, 1887. Experiments made by annealing twisted systems.

<sup>†</sup> An. 190° being, of course, the maximum hardness admissible. † Amer. Journ. [3] xxxiii. p. 28, 1887.

impaired. In the ordinary case of scratching the action is often accompanied by physical discontinuity. The interpenetration of the molecules of a viscous substance is necessarily favoured by temperature. Hence we infer the experimental result that the viscous influence of temperature is marked. If Clausius's theory of electrolysis be correct, then a certain instability or imperfect uniformity in the molecular structure of solids follows at once from the fact that many solids, notably glass \*, may be electrolyzed even at moderately high temperatures (300°).

The intensity of stress by which the above deformations are evoked was nearly constant, and equal to 0.5 kilog. on centimetre of arm. This couple, when applied to the given steel rods (radius = 0.041 centim.), is admirably adapted for the exhibition of a nearly pure viscous phenomenon, the "Nach-

wirkung" of Weber and Kohlrausch.

It is just here that certain cardinal distinctions will have to be made. According to Maxwell's view, viscosity is the same phenomenon in liquids and in solids, and the molecular mechanism by which it manifests itself quite the same in both There is nothing in Maxwell's theory to induce the reader to limit viscosity in solids to certain special changes of configuration. In solids at high temperatures, and of course in viscous fluids, there is indeed no need of such distinction, and viscosity appears as the one property into which the other configuration-properties of solid matter eventually merge. In solids, at low temperatures, on the other hand, the case is much more complex; and whereas viscosity ("Nachwirkung") still appears as a property common to solids, whether soft or hard, plastic or brittle, these ulterior distinctions—softness, hardness, plasticity (permanent set), brittleness, &c. -separate solids by very broad lines. Hence it is improbable that the whole of the mechanism, in virtue of which viscous deformations are possible in viscous fluids, is fully of the same nature as that by which viscous motion takes place in solids at ordinary temperatures. Viscosity in liquids is the mean result of divers superposed phenomena, the occurrence of any one of which, in a solid, would give rise to some special physical property of that solid. From this point of view, since viscosity is independent of the other physical properties above enumerated, and since viscosity (Nachwirkung) is common to solids without exception, I have ventured to refer it to such action between contiguous molecules as involves the least

<sup>\*</sup> Warburg, Wied. Ann. xxi. p. 622, 1884. Literary notes are there given. Warburg is able to replace six sevenths of the sodium of glass by sodium of the anode.

amount of free motion. Viscosity in solids is the result of changes of molecular configuration brought about by interchange of atoms of contiguous configurations, in the manner explained by the Clausius-Maxwell principle\*. under stress such changes take place gradually, through infinite time, because the conditions favourable to intertransfer of atoms are of rare occurrence, and because the number of molecules for which such transfer is possible is limited. This limited interchange of atoms between molecules under stress must be a property common to solids, if, according to Maxwell's conception, solids are made up of configurations in all degrees of molecular stability.

This premised, further distinction may be made. Questions arise as to whether such action can be indefinitely repeated without rupture, as in plastic solids or in viscous fluids; or whether it cannot be indefinitely repeated, as in brittle solids, &c. This indefinite repetition of the phenomenon is equivalent to a passage of molecules over or across each other, the

phraseology above used in reference to hardness.

15. The observations made in the above paragraphs relative to the visible viscous subsidence of a mechanical strain imposed on a steel rod apply for the complete explanation of the phenomenon of temper. With this purpose in view, it is merely necessary to conceive of hardening or quenching (sudden cooling of steel) as an operation by which a strain of dilatation is imparted to steel. This strain, once applied, is locked up in the metal in virtue of viscosity ‡.

The strained structure of hard steel is proved by the tendency to rupture during quenching exhibited by the metal, and by the fact that massive pieces of hard steel often explode spontaneously. The temper-strain may be studied, optically and in other ways, in glass, and at low temperatures even in

2 Aufl. 1879, p. 163.)

Again:—"Thus we may suppose that in a certain number of groups the ordinary agitation of the molecules is liable to accumulate so much that every now and then the configuration of one of the groups breaks up, and this whether it is in a state of strain or not."....

"But if a solid also contains . . . . groups of the first kind which break up of themselves . . . . " (Maxwell, l. c.)

† Cf. Am. Journ. xxxiv. pp. 1, 18, 1887.

‡ Cf. Bull. U. S. Geolog. Survey, no. 14, p. 88.

§ Batchelder, Journ. Frank. Inst. [3] viii. p. 133, 1844.

<sup>\* &</sup>quot;Betrachten wir ferner das Verhalten der Gesammt-molecüle unter einander, so glaube ich dass es auch hier zuweilen geschieht, dass das positive Theilmolecul eines Gesammt-moleculs zu dem negativen eines anderen in eine günstigere Lage kommt, als jedes dieser beiden Theilmolecüle im Augenblicke gerade zu dem anderen Theilmolecül seines eignen Gesammt-molecüls hat &c." (Mechan. Wärmtheorie, Band ii.,

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resin\*. Reckoned from the observed volume-increase due to quenching, the stress-intensity corresponding to the observed strain may be estimated at 10<sup>10</sup> dynes per square centim. in steel and 109 dynes per square centim. in glass. It is thus of the order of the respective tenacities of steel and of glass. view of the fact that the viscosity of hard steel is not above that of glasst, exceptionally great strain-intensity would not be permanently retained. Hence the secular changes of glasshard steel. At this point, moreover, the function of carbon appears. Sudden cooling from red heat induces iron and carbon to remain in the combined state, in a way favourable to the observed dilatation. Throughout the process of cooling. carbon and iron at any place within the metal are united in conformity with the given degree of carburation, and with the intensity of strain there experienced. In the cold metal, at the given place, strain is to a certain extent permanent, and independent of the strain of the surrounding medium of steel. Hence if, by gradual secular annealing of massive glass-hard steel, a sufficient number of carbon configurations are broken. stress may increase to an intensity sufficient to rupture the metal explosively.

In our earlier papers on this subject Dr. Strouhal and I were much puzzled to know whether the temper-strain, and in general the phenomena of annealing, were to be interpreted physically or chemically; whether annealing was a case of viscous subsidence of the temper-strain, or a case of mere chemical decomposition. In the light of the present advanced conceptions this distinction is superfluous. It makes no difference whether the configuration breaks up into parts chemically different (as carbon and iron, say, in steel), or into parts chemically, though not structurally, identical (as in homogeneous metals). Viscosity is conditioned by the degree of instability. Again, it is clear that the principles which account for the subsidence of the mechanical strain will also account at once for such chemical decomposition as is here in question; the difference of the two cases being vested in mere details of molecular mechanism.

16. However complex the nature of the temper-strain in steel may be, the behaviour of hard steel, when subjected

<sup>\*</sup> Marangoni, N. Cim. [3] v. p. 116, 1879 (Rupert's drops of resin); De Luynes, C. R. lxxvi. p. 346, 1873, or Phil. Mag. [4] xlv. p. 464, 1873 (Rupert's drops of glass).

<sup>†</sup> Am. Journ. xxxi. pp. 441, 443; xxxii. p. 191, 1886; xxxiii. p. 33 1887; Bull. U. S. G. S., no. 27, pp. 30 to 50, 1886.

<sup>‡</sup> Am. Journ. xxxiii. p. 30, 1887.

<sup>§</sup> Bulletin U.S. G.S., no. 35, p. 42, 1886. Structure studied by the density method, shells being consecutively removed by galvanic solution.

to the influence of change of temperature, offers sufficient proof of its occurrence. The laws of annealing \* hard steel are as follows:-

(1) The annealing-effect of any temperature acting on glass-hard steel increases gradually at a rate diminishing through infinite time; diminishing very slowly in case of low temperatures (<100°); diminishing very rapidly at first, and then again slowly at high temperatures ( $>200^{\circ}$ ); so that the highest and hardest of the states of temper possible at any given temperature is approached asymptotically.

(2) The ultimate annealing-effect of any temperature, t, is independent of the possibly pre-existing effects of the temperature  $t'^{\circ}$ , and is not influenced by subsequent applications of  $t'^{\circ}$ , provided t > t'. In the case of partial annealing at  $t^{\circ}$  (time finite), this law applies more fully as the ultimate effect of

to is more nearly reached.

Postulating the strain discussed in § 13, these laws follow at once from Maxwell's theory; and the explanation (mut. mut.) is identical in character with that given in §§ 9 to 13, with reference to the applied torsion-strain. Inasmuch as annealing is accompanied by chemical decomposition, the conditions under which the temper-strain is reduced are those of § 13.

The second law of annealing asserts that the heat-effect is analytic, but not in the same degree synthetic. The carbon configuration definitely broken up by annealing does not recombine on cooling. In a pure metal, and up to a certain limiting (small) stress, configurations broken up by stress

may recombine when stress is released or reversed.

17. In certain comparisons between the strain-effect exhibited by glass and by steel †, we were led, both by gravimetric and by polariscopic observations, to this distinction: the strain in hard steel is very perceptibly affected by annealing-temperatures as low as 50°, whereas in the case of quenched glass (Rupert's drops) perceptible annealing is incipient only at 200°. The bearing of this result on the present discussion is manifest; the difference of behaviour is due to the absence in glass of anything equivalent to the unstable carbon configuration in The case of glass is nearly that of soft steel, and the behaviour as regards viscosity in these two instances is similar.

Schroeder's important result has relevancy here; in the

‡ Wied. Ann. xxviii. p. 369, 1886,

<sup>\*</sup> Phil. Mag. [5] viii. p. 341, 1879; Wied. Ann. xi. pp. 962, 965, 967, 1880; Bull. U. S. G. S. no. 14, p. 195, 1885.
† B. and S., Amer. Journ. [3] xxxii. p. 185, 1886,

case of hard-drawn wire (Ag, Fe, and german silver) minimum viscosity is found associated with maximum susceptibility to

change of temperature.

18. Following the suggestion of § 14, it may be inferred that in the case of very complex molecular structure, instability of configuration will be a more probable occurrence than in the case of simple bodies. Conformably with this view the complex organic solids \* like silk will, cat. par., show more pronounced viscous deformation than metals or mineral solids. These known facts are thus in general accordance with Maxwell's theory. Nor is it remarkable that a complex substance like glass should lie somewhere between hard steel and soft steel in the scale of viscosity, showing therefore greater viscosity than hard steel and less viscosity than the soft non-carburized metal.

19. Maxwell's theory lends itself at once for the explanation of superposition of viscous deformations, inasmuch as the interpretation given is independent of the special peculiarity of the strain to be discussed. I will adduce a few magnetic

results which bear upon this point.

In considering the permanent effects of temperature on the residual magnetic induction in hard saturated steel, Dr. Strouhal and I † found it necessary to discriminate sharply between two species of magnetic loss:—

(1) The direct effect due simply to thermal action on the

magnetic configuration;

(2) The indirect effect due to the action of temperature in

producing mechanical annealing.

These two kinds of loss of magnetic induction often occur together. Considered separately the latter, cat. par., is very decidedly the greater in amount, and its character typified by the concemitant phenomenon of mechanical annealing. The former is not only smaller in relative magnitude, but subsides completely within a much smaller interval of time. In general, the occurrence of permanent magnetism in hard steel, in its thermal relations is subject to nearly the same laws of variation as those adduced in §§ 9 to 13 for ordinary mechanical strains. Instability of the carbon configuration is more seriously detrimental to magnetic permanence than is instability of thermal configuration.

If the unstable carbon configuration be removed by thorough annealing at 100°, then the cold, hard, resaturated magnet must show exceptionally good magnetic stability, as regards

<sup>\*</sup> Cf. for instance, Kohlrausch, Pogg. Ann. exxviii. p. 414, 1866, and many others.

† S. and B., Wied. Ann. xx. p. 662, 1883.

the effects of mean atmospheric temperature. If, now, the saturated magnet is again thoroughly annealed at 100°, the exceptionally good stability in question is even further enhanced, because the magnetic configurations unstable as far as 100° have now also been removed. The second magnetic loss has just been stated to be small. Such magnets are no longer influenced by variations of mean atmospheric temperature, nor in general by temperatures appreciably below 100°, since the rods carry the maximum of permanent hardness and the maximum of permanent magnetization corresponding to 100°. This process of consecutive annealing is the one we proposed when the magnets made are to withstand the effects of atmospheric temperature, of percussion, and of secular time\*. Cf. § 20.

20. In the above I refer to thermal, to carbon, and to magnetic configurations, using the adjectives merely to designate the cause of the instability under special consideration, whereas the configurations themselves need not necessarily be different. Thus a carbon and a thermal configuration may be one and the same grouping of atoms; so may also a thermal and a magnetic configuration. I use the latter phrase advisedly, supposing the rod showing residual magnetic induction to consist of configurations in all degrees of magnetic stability as well as in all degrees of magnetic intensity. Stability and magnetic intensity are the qualities which in the present case correspond to stability and strain respectively

in the above configurations.

Magnetic stability decreases from hard to soft and from soft steel to soft iron; following, therefore, the inverse order of viscosity. Its character, too, is different from viscosity, the tendency being toward sudden magnetic changes, even, when the cause of such change is superinduced by heat. Cf. § 19.

The mean magnetic intensity of the configuration must depend on the dimensions of the saturated rod. In the normal case of linear rods, this magnetic intensity increases from hard to soft steel†, and from steel to iron. Hence, from one point of view, carbon configurations interfere with the occurrence of intense magnetic configurations; from the other point of view, magnetic intensity increases in the direct order of viscosity, or stability of molecular configuration.

21. Summarizing the results of the above paragraphs, I believe the statement made in § 2 to be fully verified. I have shown that the effect of distributing unstable molecular con-

<sup>\*</sup> For further details, see Bull. 14, chapter vi.; or l. c. † S. and B., Wied. Ann. xx. p. 621, 1883.

figurations uniformly throughout the substance of a rigid metal like steel, is analogous to that of dissolving molecules of acid or salt in a non-conductor like pure water. These added molecules are the unstable groups with which Clausius's theory deals. In both cases the effect produced is proportional to the number of unstable molecules distributed. If the number be sufficiently increased, the medium will ultimately be a viscous fluid in the one case and an electrolytic conductor in the other. At the outset, pure water typifies the rigid solid.

The applied stress imparts a permanent strain to the solid. Viscous deformation is therefore accompanied by a residual phenomenon, which manifests itself when the applied stress is removed or reversed\*. In liquids, when acted on by electromotive forces, the analogous reaction is the reciproca-

ting force of galvanic polarization.

Again, Clausius's and Maxwell's theories mutually sustain each other. For if the conception that in a solid, molecular configurations are present in all degrees of stability is necessary to explain the behaviour of strained solid matter, it follows that configurations of more pronounced instability will be present in electrolytic systems. Conversely the fact that many solids (?) can be electrolyzed, points to the occurrence in these of a very advanced state of molecular instability. To take the concrete example of glass, the same molecular mechanism which at 300° promotes electrolytic conduction, when the solid is influenced by an electromotive force, manifests itself at low temperatures as the viscosity of the solid under stress.

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### XXI. On the Theory of Lightning-Conductors. By Prof. Oliver J. Lodge, D.Sc., LL.D., F.R.S.†

THAT a condenser discharge is oscillatory has been known ever since 1858, when Sir William Thomson's great paper "On Transient Currents" appeared. Quite recently it has been recognized, first quite explicitly perhaps, by Mr. Heaviside in the 'Electrician' for January 1885‡, that rapidly alternating currents confine themselves to the exterior of a conductor§; and Lord Rayleigh (Phil. Mag. May 1886)

† Communicated by the Author.

<sup>\*</sup> Kohlrausch, Pogg. Ann. exxviii. p. 419, 1866.

<sup>‡</sup> See also Phil. Mag. August 1886 et seq. § It is not possible, I think, to give Mr. Heaviside the credit of the

has developed an expression of Maxwell's so as to give the real resistance and inductance of a conductor for any frequency of alternation.

I propose to apply these considerations to the case of a

lightning-flash.

A lightning-flash is the discharge of a condenser through its own dielectric, and is more analogous to the bursting or the overflow of a Leyden jar than to any other laboratory phenomenon. The condenser-plates may be two clouds, or they may be a cloud and the earth. The discharge occurs mainly through broken-down air, but a lightning-rod may

form a part of its path.

The particular in which lightning transcends ordinary laboratory experiments is difference of potential or length of spark. The quantity of electricity is very moderate, the capacity of the condenser is quite small, but the potential to which it is charged is enormous. Flashes are often seen a mile long, and there is said to be a record of one seven miles long. Allowing 3000 volts to the millimetre, a mile-long spark means a potential of 16 million electrostatic units.

The capacity of a condenser with plates a square mile in area and a mile apart is roughly about \( \frac{2}{3} \) of a furlong, or say

104 centimetres.

The energy of such a condenser charged to such a potential is enormous, being over  $10^{20}$  ergs, and there is no need to assume that so much as a tenth of this is ever dissipated in

any one flash.

We may not be far wrong if we guess the capacity emptied by a considerable flash as about 10 metres or one thousandth of a microfarad. The total *charged area* is commonly much greater, but it is not all well connected, and it does not discharge all at once.

original discovery of this theorem (though doubtless he discovered it for himself), for it had been virtually anticipated by so many persons. Not counting a wide general mechanical theorem of Sir William Thomson, which may be held to include this as a special case, a great part of it is clearly indicated by Clerk-Maxwell in his paper in the Phil. Trans. for 1865. It then reappears in a more or less developed form in several papers of Lord Rayleigh, specially perhaps that in the Phil. Mag. of May 1882; and it is clearly stated for electrical oscillations in a spherical or cylindrical conductor by Prof. Horace Lamb (Phil. Trans. 1883). There are also several papers by Oberbeck, the references to which I am unable to give just now. It is certain that all these philosophers had the data at command, and could at any time have constructed the completely explicit statement; but it may be held that none of their actual statements were quite so explicit as that of Mr. Heaviside in 1885. It is well known that some ingenious experiments of Prof. Hughes first excited public interest in the matter and quickened the mathematical abstraction into life.

To make the problem a definite one consider the following case:—

An air-condenser with plates of any size separated by a distance h (height of cloud) and charged up to bursting strain ( $\frac{1}{2}$  gramme weight per square centimetre; the less strength of rare air is hardly worth troubling about). Let a small portion of this condenser, of area  $\pi b^2$ , now discharge itself; being separated from the rest after the trap-door and guardring manner. A volume of dielectric  $\pi b^2 h$  is relieved of strain, and the energy of the spark is  $E = \frac{981}{2} \pi b^2 h$  ergs.

The capacity discharged is  $S = \frac{Kb^2}{4h}$ , and the maximum potential can be reckoned by putting

$$V = \sqrt{\left(\frac{2E}{S}\right)} = \sqrt{\left(\frac{4\pi \times 981h^2}{K}\right)}$$
  
= 110h electrostatic units.

Let the discharge pass straight down the axis of the cylindrical region of length h and radius b, and let the channel occupied by it have a sectional radius a. If the path is a metal rod, then a is the sectional radius of that rod.

We have now to calculate the self-induction of such a discharge. A discharge of this kind differs from ordinary cases in having no obvious return circuit. What is happening is a conduction or disruption current down the axis of the cylindrical region considered, and an inverse displacement current in concentric cylinders all round it. I shall assume that this inverse displacement current is uniformly distributed over the whole area. A conduction rush is not uniformly distributed over the section of its conductor, but is concentrated by mutual induction of the parts towards the periphery; similarly, but inversely, there will be a tendency for the displacement currents to be stronger near the central axis than far away; but there is this difference, that whereas in a conductor currents are able to distribute themselves how they please, they will not be so free in an insulator. It is not quite correct to take the distribution as uniform, but it will not make very much difference probably. (That it is not correct may be seen by considering the initial and final stages of the dielectric. Either it is the whole of a condenser that is being discharged or it is a trap-door portion. If only a portion, the initial state is one of equal strain, but lines from surrounding charged areas spread in laterally to all the outer regions, and so finally there is an unequal distribution

of strain in it. If the whole is being discharged, then the initial state of strain is not uniform, while the final is.)

Calling the whole current down the axis  $C_0$ , we have an equal inverse displacement all over the area  $\pi(b^2-a^2)$ , so that the density of its distribution is  $\sigma$ , where  $C_0 = \pi(b^2-a^2)\sigma$ .

The intensity of magnetic force at any distance r from the

axis is

 $f = \frac{2(C_0 - C)}{r},$ 

where C is that portion of the displacement recovery which lies nearer to the axis than r. This is accurate, for the distribution of the current matters nothing so long as it is in coaxial cylinders; the portions external to r have no effect.

On the hypothesis of uniform distribution,

$$\mathbf{C} = \pi (r^2 - a^2) \sigma = \frac{r^2 - a^2}{b^2 - a^2} \mathbf{C}_0.$$

$$f = \frac{2\mathbf{C}_0}{r} \cdot \frac{b^2 - r^2}{b^2 - a^2}.$$

Hence

where the a may in practice be neglected as usually too small to matter. This is the number of lines of force through unit area at the place considered; and the whole magnetic induction in the cylindrical space considered outside the conductor is

$$h \int_{a}^{b} \mu f dr = \mu h C_0 \left( 2 \log \frac{b}{a} - 1 \right).$$

For the part inside the conductor there is an extra term to be added, which, on the hypothesis of uniform distribution in the conductor, comes out

$$\mu_0 h \int_0^a \frac{2 \frac{r^2}{a^2} C_0 dr}{r} = \mu_0 h C_0,$$

and which may really have any value between this and zero, according to the rapidity of the alternations, and the consequent deviation from uniform distribution.

The entire magnetic induction may be written LC<sub>0</sub>; hence we get the value of L, the coefficient of self-induction, or the inductance, of the circuit.

$$\mathbf{L} = h \left( 2\mu \log \frac{b}{a} - \mu + \mu_0 \right). \quad . \quad . \quad (1)$$

This I shall write for convenience  $h(\mu u^2 + \mu_0)$ , so that  $u^2$  is an abbreviation for  $\log \frac{b^2}{a^2} - 1$ \*.

<sup>\*</sup> It is quite likely that my calculation of this term u is faulty. But the truth of what follows is not affected by such an error, and a mathematician will be easily able to set it right.

In practice u may be a number not very different from 4 or 5.

Of the three terms in equation (1), the first and most important depends on no hypothesis as to distribution at all; the second depends on the assumption of uniform distribution of displacement-recoil in the dielectric, and may therefore really be greater, but not less; the third term depends on the magnetization of the conductor itself by a uniformly distributed current, and if the current keeps itself to the exterior surface, as a very rapidly alternating one will, this term vanishes.

Now that we know S and L, we can easily find the criterion for the discharge to be oscillatory, and can determine the rate of alternation.

The discharge will be oscillatory unless the resistance it meets with exceeds a certain critical value, viz.:—

$$R_0 = \sqrt{\frac{4L}{S}} = \sqrt{\frac{\frac{4h\mu u^2}{\overline{K}b^2}}{\frac{4h}{4h}}} = \frac{4h\mu u}{\sqrt{\mu K}} = \frac{4hu\mu v}{b}. \quad (2)$$

where 
$$v = \frac{1}{\sqrt{(\mu K)}}$$
 = the velocity of light =  $\frac{30}{\mu}$  ohms;

so the critical resistance is

$$R_0 = 120 \frac{h}{h} / (2 \log \frac{b}{a} - 1)$$
 ohms. . . (2')

And inasmuch as in practice h is likely to be much greater than b, and b much greater than a, this is a big resistance, which is not likely to be exceeded by the discharger. For if the line of discharge is a metallic conductor, a is moderate, but then so is R; whereas if the flash occurs through air, and it is not easy to say what the equivalent R is, then a must be considered extremely minute.

Suppose h to be a mile, b 50 metres, and a a millimetre;

 $R_0$  comes out about 15,000 ohms.

I think we shall be right in saying that this far exceeds any reasonable value that can be attributed to the resistance met with by a disruptive discharge. It is generally supposed, indeed, that a conductor and earth must have a resistance of only a few ohms, unless they are to form a considerable portion of the whole resistance a flash meets with.

In so far as the path consists of different conductors in series, it is a mere matter of summation to take them all

into account.

If the actual resistance falls greatly below the critical value

R<sub>0</sub> the discharge is thoroughly oscillatory, and the strength of the current at any instant is

$$C = \frac{V_0}{nL} e^{-mt} \sin nt, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where  $m = \frac{R}{2L}$ , and  $n^2 = \frac{1}{LS} - m^2$ . The impedance is, therefore, nL.

When the discharge is thoroughly oscillatory n is greatly bigger than m, so that the above is practically

$$C = \frac{V_0}{\sqrt{\left(\frac{L}{S}\right)}} e^{-\frac{Rt}{2L}} \sin \frac{t}{\sqrt{(LS)}}. \qquad (3')$$

The time-constant of the dying-away amplitude is  $\frac{2L}{R}$ ; the period of the alternation is  $2\pi\sqrt{(LS)}$ .

The frequency constant,

$$n = \frac{1}{\sqrt{\text{(LS)}}} = \frac{2v}{bu}, \quad . \quad . \quad . \quad (4)$$

is very great, being usually something like a million a second, more or less.

Now Lord Rayleigh has shown (Phil. Mag. May 1886) that with excessive frequencies of alternation the resistance of a conductor acquires the following greatly modified value, R being its ordinary amount,

Or, taking the permeability of the conductor the same as that of the space outside,

$$R' = \frac{1}{2n} \sqrt{(RR_0)}. \qquad (6)$$

The actual resistance is, therefore, some fraction, something like say an eighth, of the geometric mean of the ordinary resistance of the conductor and the critical resistance (2).

Under the same circumstances the value given by Rayleigh for the inductance is

L'=(L for space outside conductor) + 
$$\sqrt{\left(\frac{\mu_0 Rh}{2n}\right)}$$
,

or, as we shall now write it,

$$L' = \mu h u^2 + \frac{R'}{n}. \qquad (7)$$

The second term has to do with the magnetization of the conductor, and is, for high frequencies, very small. It is interesting as showing that of the two terms in the quantity "impedance,"

 $\checkmark (\mathbf{R}^{\prime 2} + n^2 \mathbf{L}^{\prime 2}),$ 

or, as it becomes for condenser discharges,

$$\sqrt{\left\{\frac{3}{4}R'^2+rac{L'}{S}
ight\}},$$

the second is always the larger; because, by (7),

$$nL' = R' + n\mu hu^2$$
.

Practically the second term is so much the larger that it is the only one that matters, and so

impedance = 
$$nL' = nL = n\mu hu^2 = \frac{2v\mu hu}{b} = \frac{1}{2}R_0 = \sqrt{\frac{L}{S}}$$
. (8)

or impedance =  $60 \frac{h}{b} \sqrt{\left(2 \log \frac{b}{a} - 1\right)}$  ohms. . . (8')

The total impedance, therefore, to a condenser discharge is half the critical resistance which determines whether the discharge shall be oscillatory or not; it has no important connexion with the ordinary resistance of the conductor; neither does it depend appreciably on the magnetic permea-

bility of its substance.

Hence, so long as the specific resistance of the conductor does not rise above a certain limit, its impedance depends almost entirely upon the amount of space magnetized round it and upon the capacity of the discharging condenser, and is barely at all affected either by the magnetic permeability, or the specific resistance, or even the thickness, of the conductor. The one thing that does matter is its length. True the diameter of the conductor does appear in the expression for impedance, but only under a logarithm; hence the effect of varying the thickness is only slightly felt.

The fact that impedance to a condenser-discharge is equal to half the critical resistance, or  $\sqrt{(L/S)}$ , and depends not at all upon the ordinary resistance of the discharging circuit (provided this keeps well below the critical resistance for which the discharge ceases to be oscillatory), is manifest also from

equation (3').

Thus, then, we find that a lightning-conductor offers an obstruction to a discharge as great as what a resistance of

several thousand ohms would offer to a steady current of corresponding strength; the actual obstruction being given by

equation (8').

Another way of putting the matter, is to say that for the first few oscillations the damping term,  $e^{-mt}$  in equation (3), has no appreciable effect; and that, accordingly, the E.M.F. applied to the conductor alternates rapidly from  $V_0$  to  $-V_0$  and back again.

But  $V_0$  is the initial potential of the condenser, diminished (so far as the conductor is concerned) by the E.M.F. needed to jump whatever thickness of air it has jumped before reaching the conductor. Hence this  $V_0$  may be something quite comparable to the potential needed to jump through air all the rest of the way, and it may depend on a mere nicety whether it

prefers the conductor or not.

Thus arises the difficulty experienced in helping a jar to overflow by means of discharging-tongs brought near the two coatings. Sometimes the flash will make use of the tongs, sometimes it will prefer to go all the way through air; the fact being that the obstruction offered by a metal requires a large portion of the potential needed to break through a corresponding length of air. Undoubtedly the metal rod offers some advantage; but it is much less than has been usually

supposed.

During the instant of discharge, therefore, the upper part of a lightning-rod experiences enormously high potentials in alternately opposite directions. Any conductors in the neighbourhood may easily receive side flashes, and even the bricks into which its supports are driven may be loosened and disturbed; and all this quite irrespective of any question as to the goodness or the badness of the "earth." It becomes, therefore, quite a question whether it is not, after all, advisable to try and confine the discharge to the conductor by means of insulators, or whether it is better to reduce the excessive potential by lateral extensions of considerable static capacity. The advantage of sharing the discharge among a number of well-separated conductors, instead of concentrating it all in one, is obvious.

# Theory of Experiments on "Alternative Path."

In a lecture to the Society of Arts (see Journal of the Society for 22nd June 1888, reprinted also in 'Electrician, 29th June 1888), I describe some experiments I have made on the E.M.F. needed to force a discharge through various conductors, by seeing what length of air-space it will prefer to jump. The original potential of the condenser being able to jump, say, two

inches without any alternative path, it remains able to jump, say,  $1\frac{1}{2}$  inches when offered as an alternative a copper rod a quarter of an inch thick and six or seven yards long. This gives a rough notion of the kind of results obtained, and it shows that the extremities of the rod experience almost the whole of the original E.M.F. of the condenser.

Some experiments on much the same lines had been previously made by Prof. Hughes and M. Guillemin (see Comptes rendus, 1886, Annales Télégraphiques, 1865, Address to Society of Telegraph Engineers, 1886); but they used a fine wire instead of an air-space, and tried what conductor would

protect the fine wire from being deflagrated.

Under these conditions the experiment is practically a comparison between the impedances of two conductors—one of which has its inertia term the bigger, while the other has its

resistance term the bigger.

The general theory of divided circuits has been given by Lord Rayleigh (Phil. Mag. 1886, pp. 377 et seqq.), and inasmuch as in the present case there is practically no mutual induction between the two conductors, and the frequency of . alternation is very great, the resultant resistance and induction take the following forms :-

$$R = \frac{R_1 R_2}{R_1 + R_2} + \frac{(L_1 R_2 - L_2 R_1)^2}{(R_1 + R_2)(L_1 + L_2)^2}; \quad . \quad . \quad (9)$$

The resultant impedance is, as usual,

$$P = \sqrt{\left\{\frac{3}{4}R^2 + \frac{L}{S}\right\}}$$
. . . . . . (11)

Perhaps, however, it is hardly fair to assume that the discharge will remain oscillatory when one of the branches of the divided circuit is permitted to have a high resistance. Certainly one cannot apply to such degenerate formulæ for criterion conditions.

To get the frequency these three equations must be treated simultaneously; and even so the solution is not complete, for n appears also in the true expression for  $R_1$  and  $R_2$ , so that the complete solution for a case of divided-circuit condenserdischarge is by no means simple.

The experiment with an air-gap as the alternative path is better; because one may be sure then that none of the discharge chooses that path, when it is properly adjusted for its

sparks just to fail.

# Liability of Objects to be Struck.

There are also described in my lecture to the Society of Arts, above mentioned, some experiments on the liability of objects to be struck. A distinction is drawn between two possible cases:—

(1) Where the air above the object is subjected to a steadily

increasing strain till breakdown occurs.

(2) Where the strain is thrown instantaneously upon air

and conductors with a sudden rush.

In the first case the path is prepared inductively in the air, and the breakdown occurs at the place where the tension first reaches its limiting value; this is generally on a small knob or surface, and so this is struck and carries off all the discharge independently of its resistance. If its resistance is great the flash may be feeble; if its resistance is small the flash may be noisy; but the place of occurrence of the flash is not determined by these considerations. Glow and brush discharges from points and small surfaces may readily prevent any noisy flash from occurring.

The second case is different. When a sudden rush occurs the discharge shares itself among several conductors in proportion to their impedances, quite independently of any considerations of maximum tension or prearrangement of path by induction; so that no distinction is observable between points and large knobs, in this case. Points cease to have any protective virtue; they can be struck by a noisy spark as readily as can a knob. The highest object will, in general, be struck most easily, provided its impedance is not very great. If it has a very high resistance it is barely struck at all, and it

does not then protect the others.

#### Experiment of the Recoil Kick.

Among other experiments described in the lectures above mentioned are some which appear to be of considerable theoretical interest, wherein a recoil kick is observed at the ends of long wires attached by one end to a discharging condensercircuit.

This diagram shows the arrangement.



The jar discharges at A in the ordinary way, and simultaneously a longer spark is observed to pass at B at the far end of two long leads. Or if the B ends of the wire are too far apart to allow of a spark, the wires glow and spit off brushes every time a discharge occurs at A.

The theory of the effect seems to be that oscillations occur in the A circuit according to equation (3') with a period

$$T = 2\pi \sqrt{(LS)}$$

where L is the inductance of the A circuit, and S is the capacity of the jar. These oscillations disturb the surrounding medium and send out radiations, of the precise nature of light, whose wave-length is obtainable by multiplying the above period by the velocity of propagation.

This velocity is known to be

$$v = \frac{1}{(\sqrt{\mu K})};$$

so the wave-length is

$$\lambda = vT = 2\pi \sqrt{\left\{\frac{L}{\mu} \cdot \frac{S}{K}\right\}}. \quad . \quad . \quad (15)$$

Now  $\frac{L}{\mu}$  is the electromagnetic measure of inductance, and

 $\frac{S}{K}$  the electrostatic measure of capacity. Each of these quan-

tities is of the dimension of a length, and the wave-length of the radiation is  $2\pi$  times their geometric mean.

The propagation of these oscillatory disturbances along the wires towards B goes on according to the following laws:—

Let  $l_1$  be the inductance per unit length of the wires; let  $s_1$  be their capacity, or permittance as Mr. Heaviside calls it, per unit length; and let  $r_1$  be their resistance per unit length.

Then, for the slope of potential along them, we have

$$-\frac{d\mathbf{V}}{dx} = l_1 \frac{d\mathbf{C}}{dt} + r_1 \mathbf{C}, \quad . \quad . \quad . \quad (16)$$

and for the accumulation of charge, or rise of potential with time,

$$-\frac{d\mathbf{V}}{dt} = \frac{1}{s_1} \cdot \frac{d\mathbf{C}}{dx}. \qquad (17)$$

These are equations to wave-propagation, and will give stationary waves in finite wires of suitable length, supplied with an alternating impressed E.M.F.

The solution for a long wire, for the case when  $r_1$  is small

and the frequency big \*, is

$$V = V_0 e^{-\frac{m_{1}x}{n_1}} \cos n \left(t - \frac{x}{n_1}\right) . . . . (18)$$

$$m_1 = \frac{r_1}{2l_1}, \text{ and } n_1 = \frac{1}{\sqrt{(l_1 s_1)}}.$$

where

The velocity of propagation is therefore  $n_1$ , and the wavelength is  $\frac{2\pi n_1}{n}$ .

Now, for two parallel wires as in the figure,

$$l_1 = 4\mu \log \frac{b}{a} + \frac{r_1}{n},$$

$$s_1 = \frac{K}{4 \log \frac{b}{n}},$$

and

while  $r_1$  = the geometric mean between its ordinary value and  $\frac{1}{2} n\mu_0$ ;

where the  $\mu$  and K refer to the space outside the substance of the wires,  $\mu_0$  refers to their substance, a is their sectional

radius, and b their distance apart.

The second term of  $l_1$  is, we have seen, practically zero for these high frequencies. Hence  $(n_1)$  the velocity of propagation of condenser-discharges along two parallel wires is simply the velocity of light, the same as in general space; because

 $l_1 s_1 = \mu K$ .

The pulses rush along the surface of the wires, with a certain amount of dissipation, and are reflected at the distant ends; producing the observed recoil kick at B. They continue to oscillate to and fro until damped out of existence by the exponential term in (18). The best effect should be observed when each wire is half a wave-length, or some multiple of half a wave-length, long. The natural period of oscillation in the wires will then agree with the oscillation-period of the discharging circuit, and the two will vibrate in unison, like a string or column of air resounding to a reed.

Hence we have here a means of determining experimentally the wave-length of a given discharging circuit. Either vary the size of the A circuit, or adjust the length of the B wires,

<sup>\*</sup> Mr. Heaviside has treated the problem in a much more general manner, see Phil. Mag. 1888, especially February 1888, p. 146.

until the recoil spark B is as long as possible. Then measure, and see whether the length of each wire is not equal to

$$\pi \sqrt{\left(\frac{L}{\mu} \cdot \frac{S}{K}\right)}$$

I hope to communicate some numerical results of observations made in this way to the British Association meeting at Bath.

It is interesting to see how short it is practically possible to make waves of this kind. A coated pane can be constructed of say two centimetres electrostatic capacity, and, by letting it overflow its edge, a discharge circuit may be provided of only a few centimetres electromagnetic inductance. Under these circumstances the radiated waves will be only some 20 or 30 centimetres long, corresponding to a thousand million alternations per second. Some beautiful diffraction experiments have been described by Lord Rayleigh in a recent Friday evening discourse to the Royal Institution (reprinted in 'Nature,' June 1888), and some of these might be used to concentrate the electromagnetic radiation upon some sensitive detector—possibly one of Mr. Boys's radiomicrometers, more likely some chemical detector—some precipitate or other that can be shaken out of solution by the impact of long waves, or some of Captain Abney's photographic agents.

Certainly the damping-coefficient R/2L is high, and the radiation has a very infinitesimal duration; but a rapid succession of discharges can be kept up by connexion with a

machine.

No doubt much shorter waves still may be obtained by discarding the use of any so-called condenser, and by causing the charge in a sphere or cylinder to oscillate to and fro between its ends, as might be done by giving it a succession of sparks. These oscillations, it is to be feared, however, would have too small energy to be detected by ordinary means. If they could be made quick enough to affect the retina, no doubt we could detect them with the greatest ease; but it is manifest that this can only be done by reducing the circuit to a size less than the wave-length of light. The wave-length of the electrical radiation is six times the mean of the inductance and capacity, and each of these quantities is very comparable with the linear dimensions of the conductor concerned. By setting up electric oscillations in a body as small as a molecule, no doubt they would be rapid enough to give ordinary light-waves; but the probability is that this is precisely what light-waves are.

Either the atoms are made to vibrate relatively to the

æther, by the effect of heat, and so to produce radiation; or else electrical oscillations are set up in comparatively quiescent atoms, not by heat, but by the impact of radiation from other sources, or by some organic process set in play by living protoplasm.

It is thus I would seek to explain phosphorescence and

other direct production of light from cold sources.

This direct production of light we have not yet learned artificially to accomplish; we can only heat bodies and trust to their emitting light in some unknown manner as a secondary result; but the direct process has been learnt by glowworms and Noctilucæ, and it is for us, I believe, one of the problems of the immediate future.

University College, Liverpool, July 7, 1888.

Postscript.—Since writing the above I have seen in the current July number of Wiedemann's Annalen an article by Dr. Hertz, wherein he establishes the existence and measures the length of æther waves excited by coil discharges; converting them into stationary waves, not by reflexion of pulses transmitted along a wire and reflected at its free end, as I have done, but by reflexion of waves in free space at the surface of a conducting wall.

My friend Mr. Chattock has also written to me about a recent experiment exhibited to the Physical Society, I do not know by whom, which shows that the same discharge as can excite ather waves a kilometre long can excite air waves of one millimetre. The whole subject of electrical radiation seems working itself out

splendidly.

Cortina, Tyrol, July 24, 1888.

## XXII. Notices respecting New Books.

Some Recent Works on Chemistry.

Elementary Chemistry. By M. M. Pattison Muir, M.A., and Charles Slater, M.A., M.B. Cambridge University Press. 1887.

Practical Chemistry, a course of laboratory work. By M. M. Pattison Muir, M.A., and Douglas Carnegie, B.A. Cambridge University Press. 1887.

So many manuals, text-books, and elementary treatises on Chemistry are now being issued by the teachers of the science that it becomes almost invidious to select any of these works for notice in these pages; but Mr. Pattison Muir, who is Prælector in Chemistry of Gonville and Caius College, having for some time past figured as a reformer in chemical teaching, we feel bound to call attention to the two books above named. The first of these may be described as the theoretical complement of the second work, which is the laboratory guide for those who are undergoing instruction in the principles of science in accordance with the scheme laid

down in the 'Elementary Chemistry.' There can be no doubt that our methods of teaching the science of Chemistry in this country were and are still in need of serious reform, and we gladly welcome any new departure which promises to break through the old and stereotyped system of "test-tubing" which reigned supreme in our laboratories a few years ago. The 'Elementary Chemistry' is a praiseworthy contribution to the desired reformation; but we are not very sanguine of its producing the wished for result, because the authors, in their extreme anxiety to set matters right, have rather strained the deductive method of treatment, and have handled the science in a manner which is hardly justifiable in the present state of its development. We cannot shut our eyes to the fact that Chemistry is still very largely in the descriptive stage; and any student who is taught according to a scheme which has so much of the deductive about it as that advocated by Messrs. Muir and Slater must necessarily acquire an exaggerated notion of the importance of the so-called physical principles, which are unduly pushed to the front. With respect to the companion volume on Practical Chemistry, we have only to point out that chemical teachers will find therein a large number of very suggestive experiments mixed up with a certain amount of practical instruction which the average student will, to say the least, find very difficult, if not quite impossible, to carry out in the laboratory without highly skilled supervision, and this of course greatly detracts from the value of the work. Some of the experiments are in fact culled from the original memoirs of various investigators; and we should very much question whether such practical exercises could be successfully carried out by a student without a long course of previous training. It may be that Cambridge students are exceptionally skilful, but our experience has certainly never brought us into contact with such manipulative dexterity on the part of a beginner as appears to be expected of those who are working from the 'Practical Chemistry' of Messrs. Muir and Carnegie. Although we have felt it necessary to make these strictures on the works forming the subject of the present notice, we hope that the authors will meet with better success than we have prophesied for them, because, as we have already admitted, there is ample scope for improving our systems of teaching Chemistry, and every well meant effort in this direction should be encouraged: it is only to be regretted that Mr. Muir and his coadjutors have, so to speak, overleaped themselves in their attempt at reform.

Exercises in Quantitative Chemical Analysis, with a short Treatise on Gas Analysis. By W. DITTMAR, LL.D., F.R.S. Glasgow: William Hodge and Co. 1887.

This very useful work will be found exactly what it professes to be—a laboratory guide for students who are commencing the subject of quantitative analysis. Prof. Dittmar's reputation and long experience as a practical teacher are so well established that every contribution to chemical literature from his pen is sure to be welcomed by his confrères. The present book will serve to main-

tain the author's reputation for sound and dependable practical instruction; and we have no hesitation in recommending it to all students of chemistry who wish to acquire a good all-round knowledge of the principles and methods of quantitative analysis. The first part of the volume is devoted to exercises in weighing and measuring, the fundamentals of quantitative work. The next section gives a series of exercises in analytical methods, the examples being well chosen, and sufficiently varied to give the student a broad grasp of quantitative analysis. The third section treats of organic analysis, and the fourth section of gas analysis, in connexion with which will be found some very useful exercises. next section is devoted to a series of promiscuous exercises in the application of the knowledge derived from the previous parts of the work to the analysis of certain special things likely to be met with in the course of practice; such as sea-water (upon which the author is an authority), Stassfurth Potash Salts, Cast Iron, Superphosphate, Guano, Milk, Butter, Soap, &c. The volume concludes with some useful notes. We have no doubt that Prof. Dittmar's work will soon find place among the recognized working manuals used in our laboratories.

## XXIII. Proceedings of Learned Societies.

GEOLOGICAL SOCIETY.

[Continued from vol. xxv. p. 521.]

May 23, 1888.—W. T. Blanford, LL.D., F.R.S., President, in the Chair.

THE following communications were read:—
1. "On the Spheroid-bearing Granite of Mullaghderg, Co. Donegal." By Frederick H. Hatch, Ph.D., F.G.S.

This paper deals with a remarkable variety of granite which may be compared with the well-known orbicular diorite or Napoleonite of Corsica. According to Mr. J. R. Kilroe, of the Geological Survey of Ireland, who first discovered this interesting rock, the concretionary balls occur in close juxtaposition in a mass of granite of 5 or 6 cubic yards in size. They have not been found in any

other portion of the granite area.

The author first gave a detailed description of the microscopic structure of the normal granite. It is a coarse-grained rock, composed essentially of quartz, orthoclase, microcline, oligoclase, greenish hornblende and black mica. Sphene is an accessory constituent. Since it contains no white mica, the rock belongs to that subdivision of granite which has been termed granitite. A description of the spheroidal bodies was then given. The balls are somewhat flattened, the greatest diameter being, in one case, 4 inches, the smallest 3. Each ball consists of two distinct parts, a pinkish central portion (the nucleus) and a dark-coloured peripheral or zonal portion (the shell). The nucleus consists of an irregular granitic aggregate of oligoclase felspar with a little interstitial quartz. The peripheral shell is composed chiefly of oligoclase, but also contains abundant

included plates of biotite, and over 12 per. cent. of magnetic iron-ore. It is to the presence of the last-mentioned mineral that the zonal portion owes its dark colour. By means of a Sonstadt's solution the oligoclase was isolated and analyzed with the following results:—

Sp. Gr. = 2.649

This is the composition of an oligoclase of the formula Ab<sub>3</sub>An.

The felspar of the zonal portion is disposed radially, the iron-ore radially and concentrically, while the mica appears to obey no fixed

law of arrangement.

A synopsis of the literature concerning the occurrence of similar concretionary bodies in granite was then given, the following authors being referred to:—Leopold v. Buch, Gustav Rose, Allnaud, Charpentier, Jokély, von Andrian, Zirkel, G. W. Hawes, M. de Kronstschoff, J. A. Phillips, vom Rath, Fouqué, Halst, Brögger, and Bäckström.

The conclusion the author arrived at from a consideration of the subject was, that concretionary bodies occurring in granite, may, according to the mode of arrangement of their constituents, be divided into three classes, viz.:—

1. The concretionary patches of Phillips.

The granospherites of Vogelsang.
 The belonospherites of Vogelsang.

The Spheroids from Mullaghderg belong to the last-mentioned class. They must be regarded as concretions formed, during the consolidation of the granite magma, by a process of zonal and radial crystallization around an earlier-formed nucleus.

- 2. "On the Skeleton of a Sauropterygian from the Oxford Clay, near Bedford." By R. Lydekker, Esq., B.A., F.G.S.
- 3. "On the Eozoic and Palæozoic Rocks of the Atlantic Coast of Canada in comparison with those of Western Europe and the Interior of America." By Sir J. W. Dawson, LL.D., F.R.S., F.G.S.

The author referred to the fact that since 1845 he had contributed to the Proceedings of the Geological Society a number of papers on the geology of the eastern maritime provinces of Canada, and it seemed useful now to sum up the geology of the older formations and make such corrections and comparisons as seemed warranted by the new facts obtained by himself, and by other observers of whom mention is made in the paper.

With reference to the Laurentian, he maintained its claim to be regarded as a regularly stratified system probably divisible into two or three series, and characterized in its middle or upper portion by the accumulation of organic limestone, carbonaccous beds, and iron-

ores on a vast scale. He also mentioned the almost universal prevalence in the northern hemisphere of the great plications of the crust which terminated this period, and which necessarily separate it from all succeeding deposits. He next detailed its special development on the coast of the Atlantic, and the similarity of this with that found in Great Britain and elsewhere in the west of Europe.

The Huronian he defined as a littoral series of deposits skirting the shores of the old Laurentian uplifts, and referred to some rocks which may be regarded as mere oceanic equivalents. Its characters in Newfoundland, Cape Breton, and New Brunswick were referred to. and compared with the Pebidian, &c., in England. The questions as to an Upper Member of the Huronian or an intermediate series. the Basal Cambrian of Matthew in New Brunswick, were discussed.

The very complete series of Cambrian rocks now recognized on the coast-region of Canada was noticed, in connexion with its equivalency in details to the Cambrian of Britain and of Scandinavia, and the peculiar geographical conditions implied in the absence of the Lower Cambrian over a large area of interior America.

In the Ordovician age a marginal and a submarginal area existed on the east coast of America. The former is represented largely by bedded igneous rocks, the latter by the remarkable series named by Logan the Quebec Group, which was noticed in detail in connexion with its equivalents further west, and also in Europe.

The Silurian, Devonian, and Carboniferous were then treated of and detailed evidence shown as to their conformity to the types of

Western Europe rather than to those of America.

In conclusion, it was pointed out that though the great systems of formations can be recognized throughout the Northern Hemisphere. their divisions must differ in the maritime and inland regions, and that hard and fast lines should not be drawn at the confines of systems, nor widely different formations of the same age reduced to an arbitrary uniformity of classification not sanctioned by nature. It was also inferred that the evidence pointed to a permanent continuance of the Atlantic basin, though with great changes of its boundaries, and to a remarkable parallelism of the formations deposited on its eastern and western sides.

4. "On a Hornblende-biotite Rock from Dusky Sound, New Zealand." By Captain F. W. Hutton, F.G.S.

The rock is of eruptive origin, and is associated with Archæan schists and gneisses. It is compact, crystalline, of a dark-green colour, and sp. gr. 3.00-3.07. It is composed of two minerals in nearly equal proportions, one of which, a black mica, has the two optic axes nearly coinciding. The other mineral is of a pale bluishgreen colour, and moderately dichroic; it shows an aggregate polarization of rather coarse grains, with here and there distinct crystals of considerable size. Often one side of a crystal shows a single twin, while the other side is polysynthetic. The optical characters are those of the monoclinic system, and further investigation proves these crystals to be hornblende. The mineral which shows aggregate polarization is either crushed hornblende or some altered form of it.

June 7.-W. T. Blanford, LL.D., F.R.S., President, in the Chair.

The following communications were read:—

1. The following letter from H.M. Secretary of State for India accompanying some specimens of rubies in the matrix from Burmah:—

India Office, Whitehall, S.W. 2nd June, 1888.

SIR,-

I am directed by the Secretary of State for India in Council, to present to the Geological Society some specimens of Burmese rubies attached to their matrix, which were procured by Mr. Barrington Brown, at present employed by Government in examining the mines which came into their possession on the annexation of

Upper Burmah.

Mr. Barrington Brown writes concerning these specimens thus:—
"I send \* \* six specimens of rubies in granular limestone, where
they were formed. They were obtained by blasting, under my
direction, in a place formerly mined by natives \* \* \* \*. As I
believe the fact of the ruby being traced to its matrix is new to
science, the specimens may prove of interest to scientific men \* \* \*.
I should like Professor Judd, President of the Geological Society, to
see the specimens."

I am, Sir,

Your obedient Servant, (Signed) J. A. Godley.

Professor Judd, President, Geological Society.

2. "On the Sudbury Copper Deposits (Canada)." By J. H. Collins, Esq., F.G.S.

These deposits occur in Huronian rocks. The author described two exposures, known as Copper Cliff and Stobie, about 8 miles apart. At the former the ore was found in the face of a cliff of diorite about 40 ft. high.

The ore exists in three distinct forms:—

1. As local impregnations of siliceous and felspathic beds of clastic origin, in the form of patches and strings of cupreous pyrrhotite.

2. As contact-deposits of the same material lying between

the impregnated beds and large masses of diorite.

3. As segregated veins of chalcopyrite and of nickeliferous pyrrhotite, filling fissures and shrinkage-cracks in the oremasses of the second class.

The author considered the first as original, or of high antiquity; whilst the two latter are due to segregation produced either by intrusion of diorite, or by internal movements. He compared these deposits with those of Rio Tinto of Devonian age, showing their similarities and differences. At the latter place the intrusive masses are quartz-porphyries, and the metallic deposits consist mainly of bisulphide of iron. The ore-bodies in the Canadian deposits are not so large. From the cupreous pyrrhotite of Sudbury, rich though it be, compared with the Rio Tinto ore, the copper cannot be so cheaply extracted by the wet method, and the ore is of no avail as a source of sulphur. Nickel is everywhere present in the cupreous pyrrhotite

of Sudbury, and of no advantage to the smelter. The differences above recorded are probably not due to differences in the containing rocks, since similar differences may be noticed in the pyritous deposits of Canada, where the country-rocks are identical.

3. "Notes on some of the Auriferous Tracts of Mysore Province, Southern India." By George Attwood, Esq., F.G.S., F.C.S., &c.

The author was employed during parts of 1886-7 in inspecting a large area of mineral lands in Southern India supposed to be auriferous, and the paper contained the results of his observations.

1. Melkote Section. This section (in the Hassan district of the province of Mysore), starting one mile west of Melkote in a northeasterly direction, exposed gneiss, mica-schist, hornblende-schist, quartzite, tale- and chlorite-schists, eclogite, and quartz veins, striking generally N. 20° E., and having varying dips. The eclogite was described at length, and special attention was called to the flattening of the contained garnets, which were probably originally almandite; other evidences of great crushing were also noted.

In this section and on most of the schistose lands of Mysore a dull grey, nodular, and botryoidal calcareous deposit, known as "kunkur," is found in nullahs, on hill-sides, and on the detritus of old gold washings, and it was suggested that the contained lime was

derived in great measure from hornblende-schists.

Many quartz outcrops, large at the surface but diminishing in thickness downwards, were met with at the east end of the section; these veins have a strike about N. 15° E. to N. 20° E., coincident with that of the schists.

Extensive gold-washings have been carried on in the ravines and hill-sides, and the mode of occurrence and character of the gold were described.

The author considered the schists, as well as the quartz veins, to

belong to very old series of rocks, probably Archæan.

2. Seringapatam Section. The second section was taken in a southeasterly direction from the 72nd milestone on the Seringapatam and Bangalore road to the N.W. side of the village of Arakere. Gneiss, hornblende, and mica-schists, &c., were here met with, striking about N. 20° E. with varying dips. These were traversed by auriferous quartz-veins which had been largely worked, and the author gave a description of the former methods of extracting the gold.

At the S.E. end of the section the schists were found to be much broken by porphyrite dykes of much more recent origin, most likely of Tertiary age. A small granite dyke intersected the Elliot Lode

diagonally, and was considered to be of Upper Tertiary age.

3. General Observations. The author described the results of traverses of other districts; he pointed out the evidences of great pressure which had broken up the gneissic rocks and compressed the schists, and conjectured that this might have been produced by the gradual rise of the Eastern and Western Ghats, and finally called attention to the great denudation which the Mysore plateau had undergone.

An Appendix by Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., F.G.S., gave an account of the microscopic characters of the schists, the flattened garnets, the porphyrites, &c., and in this it was pointed out that one set of rocks belonged to an ancient series which, even if wholly or in part of igneous origin, assumed their present mineral structure and condition at an epoch remote from the present, whilst another set was certainly igneous and of more recent date.

4. "On the Durham Salt-district." By E. Wilson, Esq., F.G.S.

In this paper the author described the new salt-field in the North of England, occupying the low-lying country bordering the estuary of the Tees, and situated partly in Yorkshire and partly in Durham.

The history of the rise and progress of the salt-industry in South Durham was given, since the first discovery of salt by Messrs. Bolckow Vaughan and Co. at Middlesboro', in the year 1859.

The stratigraphical position of the saliferous rocks of the Durham salt-district was considered in some detail. The diverse views which have been previously expressed on this head were referred to, and reasons given for concluding that all the beds of rock-salt which have been hitherto proved in this field, and the red rocks with which they are associated, belong to the upper portion of the Trias, viz. to the Upper Keuper series (Waterstones subdivision).

The probable area of this salt-field, the limits of the distribution and varying depths of the chief bed of rock-salt were indicated, and

the extent of its supplies pointed out.

In conclusion, the author called attention to the waste, as well as to certain other disadvantages resulting from the process of winning the salt now in operation.

- 5 "On the Occurrence of Calcisphæræ, Williamson, in the Carboniferous Limestone of Gloucestershire." By E. Wethered, Esq, F.G.S., F.C.S.
- 6. "Second Note on the Movement of Scree-Material." By C. Davison, Esq., M.A.

After briefly recapitulating the substance of his previous paper, the author now communicated the results of experiments continued for a year. He gave a figure in which a continuous line represented, in millimetres, the movements of the upper stone from week to week, whilst a contiguous dotted line indicated the mean ranges of temperature. The rate of descent does not depend solely on the mean range. He gave the following comparison of rates of descent:—

	Average daily range of	descent in	Rate of des- cent in inches
Summer, 184 days	temperature. 14°·4 F.	millim. 8	per day. •00171
Winter, 182 days	8°·0	$5\frac{1}{6}$	.00121

Thus the changes are not altogether proportional to the ranges of temperature, being relatively higher in the winter months. In

considering the influence of rain, he observed that its effects are to slightly increase the rate of descent by diminishing the coefficient of friction, and by lowering the temperature, both as being itself generally colder than the air on the ground surface, and also owing to evaporation. He likewise observed that the rate of descent was nearly doubled during the latter part of the winter, chiefly owing to the effects of snow.

#### XXIV. Intelligence and Miscellaneous Articles.

ON THE ELECTROAREOMETER. BY W. MICHELSON.

THE following very simple, but so far as I am aware unknown, experiment may serve as a good illustration of the theory

of condensers, and of the electrometer.

If the internal surface of an ordinary glass areometer is made a conductor, by being silvered for instance, it will, when dipped in a conducting liquid, obviously form a condenser of variable capacity. If the liquid and the internal coating are charged to different and constant potentials, the energy of this condenser strives towards a maximum. A force is at work which dips the areometer deeper in the liquid. The areometer sinks until the hydrostatic reaction of the liquid is so great that it can also hold in equilibrium this added force.

After a complete discharge the areometer reverts to its original

position.

If we first of all disregard the changes of capillary force due to electrification, and presuppose that the part of the areometer which projects out of the liquid is very long in comparison with the displacement of the areometer, the value of the force in question can be easily calculated from a known formula\* for the energy W of a portion of a cylindrical condenser of the length l, and the radii a and b (b > a). If the constant potentials of the coatings are A and B, this force is

 $L = \frac{\partial W}{\partial l} = \frac{K(A - B)^2}{4 \log \frac{b}{a}},$ 

where K is the dielectric constant of the kind of glass of which the areometer is constructed.

If the densities of the two liquids at whose boundary the areometer floats are  $s_1$  and  $s_2$ , then, putting the hydrostatic antagonistic force as equal to the above expression, we have for the position of equilibrium a depression

$$x = \frac{K(A-B)^{2}}{4\pi b^{2}g(s_{1}-s_{2})\log\frac{b}{a}}.$$

We see that the depression must be proportional to the square

\* Maxwell, 'Electricity and Magnetism.'

of the difference of potentials. This explains why the phenomenon is almost imperceptible at small potentials, while with greater ones there is a regular, and, under favourable circumstances, a very con-

siderable depression.

Some experiments which I have made seem to confirm the theoretical law, at any rate for not very great depressions. But with greater deflections on the contrary, (from 10 to 40 millim.), there was apparently a simple proportionality between the increases of difference of potential and the depression. This deviation may, however, be referred to the imperfection of my experiments and to different disturbing actions.

In order to keep the inner surface of the areometer in conducting communication with a source of electricity, without interfering too much with its mobility, I constructed a kind of hydrostatic balance from fine capillary tubes. A very fine silver wire passed through these tubes, and terminated at one end in the areometer, and at the

other in a separate vessel of water.

It is also very essential that the conducting liquid shall not moisten the areometer-tube, otherwise this rises against the sides on electrification, and the capacity of the condenser is increased without a perceptible depression. If ordinary water is used as conducting liquid, the air in the upper part must be replaced by an oil under which water does not moisten the glass. The sensitiveness of the apparatus is at the same time considerably increased.

After more accurate measurements the comparison of the observed and calculated depressions might give a datum for determining the alterations of capillary forces at high potentials.

If, however, this influence of the capillary forces were defined and eliminated, it might be possible to use the electroareometer as an absolute electrometer. Its indications could not however lay much claim to great accuracy.—Wiedemann's *Annalen*, No. 8b, 1888.

## ON THE SECONDARY ARCS WHICH ACCOMPANY THE RAINBOW. BY M. BOITEL.

The old theory of Descartes does not explain the formation of complementary arcs. Young, in 1804, was the first to account for the production of these arcs by means of the theory of interference. Airy showed afterwards how the position of these arcs could be determined by applying the principles of diffraction, and he fixed the position of the two former. Miller proved experimentally that Airy's theory gave very approximate results for the first two arcs. Stokes, lastly, made the calculation by a more rapid method than that of Airy, which enabled him to obtain the position of the first fifty bands.

But Airy in his calculation assumed that the equation of the emergent wave (which is shaped like the letter S) in reference to the tangent, and the normal to the curve at the point of inflexion  $y = \frac{x^3}{3a^2}$ , and he has not given the expression for the constant  $a^2$ .

I have succeeded in finding the exact equation of the emergent wave and comparing it with that of Airy. I have deduced from it the value of the coefficient  $a^2$  for a rainbow of the order K,

$$a^2 = R^2 \frac{\cos^3 I(K+1)^2}{\sin IK(K+2)};$$

as a particular case we have for the first bow,

$$\alpha^2 = \frac{4}{3} R^2 \frac{\cos^3 I}{\sin I},$$

R being the radius of the sphere of liquid, and I the angle of incidence of the ray of light of minimum deflection.

By the help of this value it will be found that the deflection of a complementary band is given by the formula

$$\tan \theta = \frac{m}{(54)^{\frac{1}{3}}} \frac{(\lambda^2 \sin I)^{\frac{1}{3}}}{\cos I} \frac{I}{R^{\frac{2}{3}}},$$

m being the number calculated by Stokes which refers to the band

in question, and  $\lambda$  the wave-length of the light employed.

Comparing the numbers obtained experimentally by Miller with those furnished by the last equation, I have found a disagreement which increases with the number of the order of the band in question. I have likewise compared with the theory the experiments recently made by Pülfrich on glass cylinders, and I have found the same want of agreement.

The theory of Airy appears thus to need supplementing. For this purpose the position of the supplementary bands must be determined by the aid of the exact equation for the emergent wave which I have obtained, and the results be compared with those obtained by

experiment.

But the preceding formula shows that the deflection of a band is greater the smaller the radius of the drop or cylinder, and the feebler the index. In order to produce experimentally cylinders of very small index, I had recourse to liquid veins which I caused to jet vertically inside a rectangular glass trough filled with a liquid which did not mix with the former, and of an index nearly the same. While a thread of water in air gives between the two former supernumerary bands a deviation of 40°, a thread of petroleum jetting into water enables us to obtain a deflection of 2° between these two bands; ether, lastly, under the same conditions gives more than 5°.

But these experiments present great difficulties owing to the instability of the vein. Thus I now use small cylinders of crown glass with a radius of about 0.4 millim., and which I place vertically in the centre of the trough filled with liquid. These experimental determinations amplify the angular distance of the bands, and increase the accuracy of the measurements.

They have enabled me to prove that for great deflections the discrepancy between theory and observation only increases. Airy's theory is then only a first approximation, and I hope soon to be in a position to introduce into it the necessary corrections.—Comptes

rendus, May 28, 1888.

#### LONDON, EDINBURGH, AND DUBLIN

## PHILOSOPHICAL MAGAZINE

AND

### JOURNAL OF SCIENCE.

[FIFTH SERIES.]

#### SEPTEMBER 1888.

XXV. On the Reflexion of Light at a Twin Plane of a Crystal. By Lord Rayleigh, Sec. R.S.\*

MY object in the present paper is to calculate à priori the reflexion of light at the surface between twin crystals, and to obtain formulæ analogous to those discovered by Fresnel for the case where both media are isotropic. It is evident that success can only be attained upon the basis of a theory capable of explaining at once Fresnel's laws of double refraction in crystals and those just referred to, governing the intensity of reflexion when light passes from one isotropic medium to another. So far as I am aware the electric theory of Maxwell is the only one satisfying these conditions; and I have accordingly employed the equations of this theory. It will be remembered that the electric theory of double refraction was worked out by Maxwell himself, and that the application to the problem of reflexion was successfully effected by von Helmholtz and Lorentz ‡. The present investigation starts, however, independently from the fundamental equations, as given in Maxwell's 'Electricity and Magnetism.'

\* Communicated by the Author.

1 References to the works of previous writers will be found in Glaze-

brook's Report on Optical Theories, Brit. Assoc. Rep. 1886.

<sup>†</sup> See Prof. Willard Gibbs's excellent "Comparison of the Elastic and the Electrical Theories of Light with respect to the Law of Double Refraction and the Dispersion of Colours" (Am. Journ. Sci. June 1888), which reaches me while revising the present investigation for the press.

Equations of a Dielectric Medium, of which the Magnetic Permeability is Unity throughout.

In Maxwell's notation the various components are represented as follows:—

and the equations connecting them may be written

$$u = \frac{df}{dt}$$
,  $v = \frac{dg}{dt}$ ,  $w = \frac{dh}{dt}$ , . . . (1)

$$\frac{df}{dx} + \frac{dg}{dy} + \frac{dh}{dz} = 0, \dots (2)$$

$$4\pi u = \frac{dc}{dy} - \frac{db}{dz}, \quad 4\pi v = \frac{da}{dz} - \frac{dc}{dx}, \quad 4\pi w = \frac{db}{dx} - \frac{da}{dy}, \quad . \quad . \quad (3)$$

$$a = \frac{dH}{dy} - \frac{db}{dz}, \qquad b = \frac{dF}{dz} - \frac{dH}{dx}, \qquad c = \frac{db}{dx} - \frac{dF}{dy}, \quad . \quad (4)$$

$$P = -\frac{dF}{dt} - \frac{d\Phi}{dx}, \quad Q = -\frac{dG}{dt} - \frac{d\Phi}{dy}, \quad R = -\frac{dH}{dt} - \frac{d\Phi}{dz}. \quad (5)$$

In (1) it is assumed that the medium is a perfect insulator. Equations (4) and (5) may be replaced by

$$\frac{da}{dt} = \frac{dQ}{dz} - \frac{dR}{dy}, \quad \frac{db}{dt} = \frac{dR}{dx} - \frac{dP}{dz}, \quad \frac{dc}{dt} = \frac{dP}{dy} - \frac{dQ}{dx}, \quad (6)$$

from which  $\Phi$  disappears. Thus

$$4\pi \frac{d^{2}f}{dt^{2}} = 4\pi \frac{du}{dt} = \frac{d}{dy} \frac{dc}{dt} - \frac{d}{dz} \frac{db}{dt}$$

$$= \frac{d^{2}P}{dy^{2}} + \frac{d^{2}P}{dz^{2}} - \frac{d}{dx} \left\{ \frac{dQ}{dy} + \frac{dR}{dz} \right\}$$

$$= \nabla^{2}P - \frac{d}{dx} \left\{ \frac{dP}{dx} + \frac{dQ}{dy} + \frac{dR}{dz} \right\} \qquad (7)$$

where as usual

$$\nabla^2 = d^2/dx^2 + d^2/dy^2 + d^2/dz^2.$$

In (7) and the similar equations in g and h there is involved no assumption as to the homogeneity or isotropy of the

dielectric medium. If, however, these conditions are fulfilled,

$$\frac{d\mathbf{P}}{dx} + \frac{d\mathbf{Q}}{dy} + \frac{d\mathbf{R}}{dz} = 0,$$

P, Q, R being proportional to f, g, h; and the equations then

assume a specially simple form.

The boundary conditions which must be satisfied at the transition from one homogeneous medium to another are obtained without difficulty from the differential equations. We will suppose that the surface of transition is the plane x=0. The first condition follows immediately from (2). It is that f must be continuous across the surface x=0. Equation (7) shows that dQ/dy + dR/dz must be continuous. From the similar equation in g, viz.:—

we see not only that dc/dt, or c, must be continuous, but also that Q must be continuous. In like manner from the corresponding equation in h it follows that R and b must be continuous. The continuity of Q and R secures that of dQ/dy + dR/dz; so that it is sufficient to provide for the continuity of

$$f, Q, R, b, c. . . . . . . (A)*$$

#### Isotropic Reflexion.

If both media are isotropic the problem of reflexion of plane waves is readily solved. When the electric displacements are perpendicular to the plane of incidence (xy), f and g vanish, while h and the other remaining functions are independent of z. The only boundary conditions requiring attention are that R and b should be continuous, or by (6) that R and dR/dx should be continuous. This leads, as is well known, to Fresnel's sine-formula as the expression for the reflected wave.

When the electric displacements are in the plane of incidence, h=0, and (as before) all the remaining functions are independent of z. As an introduction to the more difficult investigation before us, it may be well to give a sketch of the solution for this case. In the upper medium we have as the

<sup>\*</sup> Of these conditions the first is really superfluous. If we differentiate (7) &c. with respect to x, y, z respectively and add, we see that the truth of (2) is involved. In some cases it would shorten the analytical expressions if we took P, Q, R as fundamental variables, in place of f, g, h.

relation between force and displacement,

P, Q, 
$$R = 4\pi V^2(f, g, h)$$
, . . . (9)

and in the lower,

P, Q, R=
$$4\pi V_1^2(f, g, h)$$
, . . . (10)

V,  $V_1$  being the two wave-velocities, whose ratio gives the refractive index. Since h=0, R=0; and since R=0, dP'dz=0, it follows by (6) that b=0. The only conditions (A) requiring further consideration are thus the continuity of f, Q or  $V^2g$ , and c.

As the expression for the incident wave we take

$$f = q e^{i(px+qy+st)}, \quad g = -p e^{i(px+qy+st)}, \quad . \quad . \quad . \quad (11)$$

the ratio of the coefficients being determined by the consideration that the directions f, g, h and p, q, r are perpendicular \*. In like manner for the reflected wave we have

$$f = q \theta' e^{i(-px+qy+st)}, \quad g = p \theta' e^{i(-px+qy+st)}, \quad . \quad (12)$$

and for the refracted wave

$$f = q \theta_1 e^{i(p_1 x + qy + st)}, \quad g = -p_1 \theta_1 e^{i(p_1 x + qy + st)}.$$
 (13)

The coefficient of y is the same for all the waves, since their traces on the plane x=0 must move together. The multipliers  $\theta'$ ,  $\theta_1$  determine the amplitudes of the reflected and refracted waves, and may be regarded as the quantities whose expression is sought. The velocity of propagation in the first medium is  $s/\sqrt{(p^2+q^2)}$ , so that

We have now to consider the boundary conditions. The continuity of f, when x=0, requires that

$$1+\theta'=\theta_1; \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and the continuity of  $\nabla^2 g$  requires that

$$\nabla^2 p (1-\theta') = \nabla_1^2 p_1 \theta_1.$$
 . . . (16)

These two equations suffice for the determination of  $\theta'$ ,  $\theta_1$ ; and we may infer that the third boundary condition is superfluous. It is easily proved to be so; for in the upper medium,

$$\begin{aligned} \frac{dc}{dt} &= \frac{dP}{dy} - \frac{dQ}{dx} = V^2 \left\{ \frac{df}{dy} - \frac{dg}{dx} \right\} \\ &= V^2 (1 + \theta^I) \left( p^2 + q^2 \right) e^{i(qy + st)} \end{aligned}$$

<sup>\*</sup> In the present case r=0.

when x=0. In the lower medium, when x=0,

$$\frac{dc}{dt} = \nabla_1^2 \theta_1 (p_1^2 + q^2) e^{(qy+st)}$$
;

so that by (14) the continuity of dc/dt leads to the same condition as the continuity of f.

The usual formula for the reflected wave is readily obtained from (15), (16). If  $\phi$ ,  $\phi_1$  be the angles of incidence and refraction,

$$V_1^2/V^2 = \sin^2\phi_1/\sin^2\phi,$$
  
 $p_1/p = (p_1/q) \div (p/q) = \cot \phi_1/\cot \phi;$ 

so that

$$\frac{1-\theta'}{1+\theta'} = \frac{\sin^2\phi_1 \cot \phi_1}{\sin^2\phi \cot \phi} = \frac{\sin 2\phi_1}{\sin 2\phi}.$$

Accordingly,

$$\theta' = \frac{\sin 2\phi - \sin 2\phi_1}{\sin 2\phi + \sin 2\phi_1} = \frac{\tan (\phi - \phi_1)}{\tan (\phi + \phi_1)}. \qquad (17)$$

The insertion of this value of  $\theta'$  in (12) gives the expression for the reflected wave corresponding to the incident wave (11). The ratio of amplitudes in the two cases, being proportional to  $\checkmark(f^2+g^2)$ , is represented by  $\theta'$ , and (17) is the well-known tangent-formula of Fresnel.

#### Propagation in a Crystal.

In a homogeneous crystalline medium, the relation of force to strain may be expressed

P, Q, R=
$$4\pi(a_1^2f, b_1^2g, c_1^2h)$$
 . . (18)

where  $a_1$ ,  $b_1$ ,  $c_1$  are the principal wave-velocities. We here suppose that the axes of co-ordinates are chosen so as to be parallel to the principal axes of the crystal. The introduction of these relations into (7), &c., gives

$$d^{2}f/dt^{2} = a_{1}^{2} \nabla^{2}f - d\Pi/dx d^{2}g/dt^{2} = b_{1}^{2} \nabla^{2}g - d\Pi/dy d^{2}h/dt^{2} = c_{1}^{2} \nabla^{2}h - d\Pi/dz$$
, (19)

where

$$\Pi = a_1^2 df/dx + b_1^2 dg/dy + c_1^2 dh/dz \quad . \quad . \quad (20)$$

The principal problem of double refraction is the investigation of the form of the wave-surface. By means of (19) we can readily determine the law of velocity (V) for various directions of wave-front (l, m, n). For this purpose we assume

where

$$\boldsymbol{\omega} = lx + my + nz - \nabla t, \quad . \quad . \quad . \quad . \quad (22)$$

and  $k=2\pi$  ÷ wave length. In accordance with (2) we must have

$$l\lambda + m\mu + n\nu = 0, \dots \dots (23)$$

signifying that the electric displacement is in the plane of the wave-front. If we now write

$$\Pi = \Pi_0 e^{ik\omega},$$

and substitute the values of f, g, h from (21) in (19) we find

$$\lambda (\nabla^2 - a_1^2) = ik^{-1}\Pi_0 \cdot l$$
, &c.,

so that by (23)

$$\frac{l^2}{\mathbf{V}^2 - a_1^2} + \frac{m^2}{\mathbf{V}^2 - b_1^2} + \frac{n^2}{\mathbf{V}^2 - c_1^2} = 0, \quad . \quad . \quad . \quad (24)$$

which is Fresnel's law of velocities, leading to the wave-surface discovered by him.

#### Reflexion at a Twin Plane.

We are now prepared for the consideration of our special problem, viz., the reflexion of plane waves at a twin surface of a crystal. We suppose that the plane of separation is x=0, and we assume that there is a plane perpendicular to this (z=0), with respect to which each twin is symmetrical. The only difference between the two media is that which corresponds to a rotation through 180° about the axis of x, perpendicular to the twin plane.

In consequence of the symmetry the axis of z is a principal axis in both media; but the axes of x and y are not principal axes. For the relation between force and strain in the first

medium we may take

$$P=4\pi(Af+Bg), Q=4\pi(Bf+Cg), R=4\pi Dh.$$
 (25)

In the second medium we may in the first instance assume similar expressions with accented letters; but the peculiar relation between the two media demands that A'=A, C'=C, D'=D, B'=-B. Thus for the second twin medium,

$$P=4\pi (Af-Bg), Q=4\pi (-Bf+Cg), R=4\pi Dh, . (26)$$

the only difference being the change in the sign of B. If B vanish, all optical distinction between the twins disappears, and there can be no reflexion. The magnitude of B depends upon the intensity of the double refraction in the twins, and also upon the angles between the principal axes and the twin

plane. If one of these angles were to vanish, B would dis-

appear, in spite of a powerful double refraction.

For a general solution of the problem of reflexion from a twin plane, we should have to suppose the plane of incidence to be inclined at an arbitrary angle to the plane of symmetry (x,y); but we may limit ourselves without much loss of interest to the two principal cases, when the plane of incidence (1) coincides with the plane of symmetry, (2) is perpendicular to it.

#### Incidence in the Plane of Symmetry.

Under the first head there are two problems which may be considered separately. The simplest is that which arises when the vibrations are perpendicular to the plane of incidence, that is, are parallel to z. It is not difficult to see that in this case the difference between the twins never comes into operation, and that accordingly the reflexion vanishes; but it may be well to apply the general method.

Since f, g, and therefore [by (25), (26)] P and Q, vanish throughout, while h and R are independent of z, the two first of equations (7) are satisfied identically, and the third becomes

$$4\pi \frac{d^{2}h}{dt^{2}} = \frac{d^{2}R}{dx^{2}} + \frac{d^{2}R}{dy^{2}},$$
or by (25)
$$\frac{d^{2}h}{dt^{2}} = D\left(\frac{d^{2}h}{dx^{2}} + \frac{d^{2}h}{dy^{2}}\right). \qquad (27)$$

This equation applies to both media, since there is no change in the value of D. Thus, so far as the equations to be satisfied in the interior are concerned, the incident wave may be supposed to continue its course without alteration.

It is equally evident that the general boundary conditions are also satisfied. For f, Q, c vanish throughout, and by (6) the continuity of R and b merely requires the continuity of h and dh/dx. Since all the conditions are satisfied by supposing the incident wave to pass on without alteration, it is clear that there can be no reflected wave.

We have next to consider the case when the vibrations are executed in the plane of incidence, so that h vanishes, while (as before) all the remaining functions are independent of z. On account of the symmetry there can be but one reflected and but one refracted wave, and in each h must vanish. We may, therefore, take the following expressions as applicable to the various waves:—

Incident wave:

$$f = q e^{i(px+qy+st)}, \quad g = -p e^{i(px+qy+st)}$$
 . (28)

satisfying

$$pf+qg=0$$
;

Reflected wave:

$$f = q \theta' e^{i(p'x + qy + st)}, \quad g = -p' \theta' e^{i(p'x + qy + st)}$$
 . (29)

Refracted wave:

$$f = q \theta_1 e^{i(p_1 x + qy + st)}, \quad g = -p_1 \theta_1 e^{i(p_1 x + qy + st)}$$
. (30)

The coefficient of the time (s) is necessarily the same throughout on account of the periodicity; and the coefficient of y is the same, since the traces of all three waves upon the plane of separation x=0 must move together. The relations between  $p, q, s; p', q, s; p_1, q, s$  are to be obtained by substitution in the differential equations. Of these the equation in h is satisfied identically, since R=0. The other equations for the upper medium are by (7), (8), (25),

$$\frac{d^2f}{dt^2} = \frac{d^2}{dy^2} (Af + Bg) - \frac{d^2}{dx \, dy} (Bf + Cg),$$

$$\frac{d^2g}{dx^2} = \frac{d^2}{dx^2} (Af + Bg)$$

$$\frac{d^2g}{dt^2} = \frac{d^2}{dx^2} (Bf + Cg) - \frac{d^2}{dx \, dy} (Af + Bg).$$

These must be satisfied by the incident and reflected waves. On substitution we find that both equations lead to the same conditions, viz.:—

 $s^2 = Aq^2 - 2Bpq + Cp^2$ , . . . (31)

a quadratic equation of which the two roots give p and p' in terms of q and s.

In the second medium we get in like manner for the re-

fracted wave

or

$$s^2 = Aq^2 + 2Bp_1q + Cp_1^2$$
, . . . (32)

the sign of B being changed. Equating the two values of  $s^2$ , we find

We have now to consider the boundary conditions (A). The functions R and b vanish throughout; but it remains to provide for the continuity of f, Q, and c, when x=0. The first of these conditions gives at once

$$1+\theta'=\theta_1. \quad . \quad . \quad . \quad . \quad (34)$$

Again, the continuity of Q, equal to Bf + Cg in the first

medium, and to -Bf+Cg in the second, gives

$$Bq - Cp + \theta' (Bq - Cp') = -\theta_1 (Bq + Cp_1). \qquad (35)$$

The continuity of c leads, when regard is paid to (31), (32), merely to the repetition of the condition (34).

If we eliminate  $\theta_1$  between (34), (35), we find

$$\theta'\{2Bq - Cp' - Cp_1\} = C(p - p_1) - 2Bq = 0$$
 by (33).

Hence  $\theta'$  vanishes. Neither in this case, nor when the vibrations are perpendicular to the plane of incidence, is there any reflexion of light incident in the plane of symmetry. And this conclusion may of course be extended to natural light, and to light plane or elliptically polarized in any way whatever.

Plane of Incidence perpendicular to that of Symmetry.

We have now to consider the case when the plane of incidence is the plane y=0, perpendicular to that of symmetry. Here f, g, h are all finite, but they (as well as P, Q, R, &c.) are independent of the coordinate y. The problem is more complicated than when the plane of incidence coincides with that of symmetry, because an incident wave is here attended by two reflected waves, and two refracted waves.

The equation of the incident wave in the upper medium

may be expressed

$$f, g, h = (\lambda, \mu, \nu) e^{i(px+rz+st)};$$
  
or, since by (2)  $\lambda p + \nu r = 0,$   
 $f, g, h = (r, \mu, -p) e^{i(px+rz+st)}.$  . . . (36)

The differential equations to be satisfied in the upper medium assume the form

$$\begin{split} \frac{d^2f}{dt^2} &= \frac{d^2}{dz^2} (\mathbf{A}f + \mathbf{B}g) - \frac{d^2}{dx \, dz} (\mathbf{D}h), \\ \frac{d^2g}{dt^2} &= \left(\frac{d^2}{dx^2} + \frac{d^2}{dz^2}\right) (\mathbf{B}f + \mathbf{C}g), \\ \frac{d^2h}{dt^2} &= \frac{d^2}{dx^2} (\mathbf{D}h) - \frac{d^2}{dx \, dz} (\mathbf{A}f + \mathbf{B}g). \end{split}$$

If we substitute for f, g, h from (36), the first and third equations give

 $s^2 = r(Ar + B\mu) + p^2D$ , . . . (37)

and the second equation gives

$$\mu s^2 = (p^2 + r^2) (Br + C\mu)$$
. . . . (38)

These two equations determine p and  $\mu$ , when r, s are given. Since the elimination of  $\mu$  leads to a quadratic in  $p^2$ , it is evident that there are four admissible values  $\pm p_1$ ,  $\pm p_2$ , corresponding to waves of given periodicity, whose trace on the plane of separation moves with a given velocity. Of these two (say with the + sign) are waves approaching the surface, and two are waves receding from it. If we limit ourselves to a single incident wave  $(+p_1)$ , we shall have still to take into account two reflected waves corresponding to  $-p_1, -p_2$ . The equations show that the value of  $\mu$  is the same whether p be positive or negative; we shall suppose that  $\mu_1$  corresponds to  $\pm p_1$ ,  $\mu_2$  to  $\pm p_2$ .

In applying the equations to the second medium we have to change the sign of B; and it is evident that they are satisfied by the same values of p as before, and that the preceding values of  $\mu$  are to be taken negatively. Hence in the second medium  $-\mu_1$  corresponds to  $\pm p_1$ ,  $-\mu_2$  to  $\pm p_2$ . For the purposes of our present problem, where there is no incident wave in the second medium, we are concerned only

with  $+ p_1$  and  $+ p_2$ .

The complete specification of the system of waves corresponding to a single incident wave  $(p_1)$  in the first medium is thus:—

Incident wave:

$$f, g, h = (r, \mu_1, -p_1) \Theta_1 e^{i(p_1 x + rz + st)}; \dots$$
 (39)

Two reflected waves:

Two refracted \* waves:

$$\begin{split} f,\,g,\,h &= (r,-\mu_1,-p_1) \,\,\theta_1 \, e^{i(p_1x+rz+st)} \\ &+ (r,-\mu_2,-p_2) \,\,\theta_2 \, e^{i(p_2x+rz+st)}. \end{split} \label{eq:formula} \tag{41}$$

The next step is the introduction of the boundary conditions (A). The continuity of f requires that

$$\Theta_1 + \theta' + \theta'' = \theta_1 + \theta_2$$
. . . . (42)

The continuity of R, or Dh, or h, gives with equal facility

$$p_1\Theta_1 - p_1\theta' - p_2\theta'' = p_1\theta_1 + p_2\theta_2.$$
 (43)

Again, the continuity of Q, equal to Bf + Cg in the first

<sup>\*</sup> It should be noticed that one of the refracted waves is not refracted in the literal sense, being parallel to the incident wave.

medium and to -Bf+Cg in the second, gives

$$(Br + C\mu_1)\Theta_1 + (Br + C\mu_1)\theta' + (Br + C\mu_2)\theta''$$

$$= -(Br + C\mu_1)\theta_1 - (Br + C\mu_2)\theta_2. . . (44)$$

The continuity of b, or db/dt, or by (6) dR/dx-dP/dz, is found, when regard is paid to (37), to be already secured by (42); and we have only further to consider the continuity of dc/dt, or by (6) of dQ/dx, since P is here independent of y. Thus

$$p_{1}(Br + C\mu_{1})\Theta_{1} - p_{1}(Br + C\mu_{1})\theta' - p_{2}(Br + C\mu_{2})\theta''$$

$$= -p_{1}(Br + C\mu_{1})\theta_{1} - p_{2}(Br + C\mu_{2})\theta_{2}. \qquad (45)$$

The coefficients which occur in (44), (45) may be expressed more briefly in terms of the *velocities* of the various waves. For

$$V^2 = s^2/(p^2 + r^2)$$
, . . . . . . (46)

and thus by (38),

$$Br + C\mu_1 = \mu_1 V_1^2$$
,  $Br + C\mu_2 = \mu_2 V_2^2$ . (47)

Setting now

$$p_2/p_1 = \varpi$$
,  $\mu_2 V_2^2/\mu_1 V_1^2 = \sigma$ , . . (47')

the four equations of condition take the form

$$\Theta_{1} + \theta' + \theta'' = \theta_{1} + \theta_{2}, 
\Theta_{1} - \theta' - \varpi \theta'' = \theta_{1} + \varpi \theta_{2}, 
\Theta_{1} + \theta' + \sigma \theta'' = -\theta_{1} - \sigma \theta_{2}, 
\Theta_{1} - \theta' - \varpi \sigma \theta'' = -\theta_{1} - \varpi \sigma \theta_{2}.$$
(48)

If we equate the values of  $\theta_1$ ,  $\theta_2$  obtained from the first and second pairs of equations (48), we find

$$(\sigma+1)\theta' + (\varpi+1)\sigma\theta'' = 0, (\varpi-1)\Theta_1 + (\varpi+1)\theta' + \varpi(\sigma+1)\theta'' = 0,$$
 (49)

and from these again

$$\theta' = -\frac{\sigma(\varpi^2 - 1)\Theta_1}{(\varpi - \sigma)(\varpi\sigma - 1)}, \quad . \quad . \quad . \quad (50)$$

$$\theta'' = \frac{(\sigma+1)(\varpi-1)\Theta_{1}}{(\varpi-\sigma)(\varpi\sigma-1)}, \quad . \quad . \quad . \quad (51)$$

by which the two reflected waves are determined.

These reflected waves correspond to the incident wave  $(\Theta_1, p_1, \mu_1)$ , and it is the wave  $\theta'$  which is reflected according to the ordinary law. If there be a second incident wave  $(\Theta_2, p_2, \mu_2)$ , the corresponding reflected waves are to be found from (50), (51) by interchanging  $\theta'$ ,  $\theta''$ , and by writing for  $\varpi$ ,  $\sigma$  the reciprocals of these ratios. If both incident waves

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coexist,

$$\theta' = \frac{(1-\varpi)\sigma}{(\varpi-\sigma)(\varpi\sigma-1)} \{ (1+\varpi)\Theta_1 + \varpi(1+\sigma)\Theta_2 \}, . (52)$$

$$\theta^{\prime\prime}\!=\!\frac{\varpi\!-\!1}{(\varpi\!-\!\sigma)(\varpi\sigma\!-\!1)}\left\{(1\!+\!\sigma)\Theta_1\!+\!(1\!+\!\varpi)\sigma\Theta_2\right\}\!. \ . \ (53)$$

It will be observed that although the fronts of the two incident waves  $\Theta_1$ ,  $\Theta_2$  are not parallel, they are the waves that would be generated by the double refraction of a single wave incident from an isotropic medium upon a face of the crystal parallel to the twin plane.

#### Doubly Refracting Power small.

Thus far our equations are general. But the interpretation will be very much facilitated if we introduce a supposition, which does not deviate far from the reality of nature, viz. that the doubly refracting energy is comparatively small. There is no new limitation upon the direction of the principal axes relatively to those of coordinates, but we assume that A, C, D are nearly equal, and that B is small. We may imagine the two twin crystals to be bounded by faces parallel to the twin face, and to be embedded in an isotropic medium of nearly similar optical power. Under these circumstances  $p_1$ ,  $p_2$ ;  $V_1$ ,  $V_2$  are nearly equal, so that approximately  $\varpi=1$ ,  $\sigma=\mu_2/\mu_1$ ; and we may write (52), (53) in the form

$$\theta' = \frac{p_2 - p_1}{p(\mu_2 - \mu_1)^2} \left\{ 2\mu_1 \mu_2 \Theta_1 + \mu_2 (\mu_1 + \mu_2) \Theta_2 \right\}, \quad . \quad (54)$$

$$\theta'' = \frac{p_1 - p_2}{p(\mu_2 - \mu_1)^2} \left\{ \mu_1(\mu_1 + \mu_2)\Theta_1 + 2\mu_1\mu_2\Theta_2 \right\}. \quad . \quad (55)$$

It should be remarked that the intensities of the waves represented by  $\Theta_1$  &c. are not simply proportional to  $\Theta_1^2$ , &c. Referring to (39), (40), we see that the intensity of  $\Theta_1$ ,  $\theta'$  is measured by  $(r^2 + p^2 + \mu_1^2)(\Theta_1^2, \theta'^2)$ ; and that of  $\Theta_2$ ,  $\theta''$  by  $(r^2 + p^2 + \mu_2^2)(\Theta_2^2, \theta''^2)$ .

#### Plate bounded by Surfaces parallel to Twin Plane.

Let us now regard the waves  $\Theta_1$ ,  $\Theta_2$  as due to the passage into the crystal of waves from an isotropic medium, under such conditions (of gradual transition, if necessary) that there is no loss by reflexion. The interface is supposed to be parallel to the twin reflecting plane, and the optical power to be so nearly equal to that of the crystal that the refraction is negligible. Then, if the vibration parallel to y (perpendicular to the condition of the crystal that the refraction is negligible.

dicular to the plane of incidence) be M, and that in plane of incidence be N, we have

$$\mathbf{M} = \mu_1 \Theta_1 + \mu_2 \Theta_2, \quad . \quad . \quad . \quad . \quad (56)$$

$$N = \sqrt{(p^2 + r^2)} \{\Theta_1 + \Theta_2\}.$$
 (57)

In like manner, if the vibrations of the emergent reflected wave perpendicular and parallel to the plane of incidence be M', N',

$$M' = \mu_1 \theta' + \mu_2 \theta'', \dots (58)$$

$$N' = \sqrt{(p^2 + r^2)} \{\theta' + \theta''\}.$$
 (59)

If we are prepared to push to an extreme our supposition as to the smallness of the doubly refracting power,  $\Theta$ ,  $\theta$  in these equations may be identified with the corresponding quantities in (54), (55); for a retardation of phase in crossing and recrossing the stratum alike for all the waves might be disregarded. We shall presently return to this question; but we will in the meantime trace out the consequences which ensue when the double refraction, if not extremely small in itself, is at least so small in relation to the distances through which it acts (the thickness of the stratum), that the relative changes of phase may be neglected. Then

We have now to introduce certain relations derived from (37), (38). By elimination of s, we get

Br. 
$$\mu^2 + \mu \{(A-C)r^2 + (D-C)p^2\} - Br(p^2 + r^2) = 0$$
. (62)

If we here disregard the difference between  $p_1$  and  $p_2$ , we may treat it as a quadratic, by which the two values of  $\mu$  are determined; and it follows that

$$-\mu_1\mu_2 = p^2 + r^2$$
. . . . . . (63)

We might have arrived at this conclusion more quickly from the consideration that in the limit the two directions of displacement  $(r, \mu_1, p_1)$ ,  $(r, \mu_2, p_2)$  in the reflected waves must be perpendicular to one another.

Again, from the general equation (37) we see that

$$Br(\mu_1 - \mu_2) + (p_1^2 - p_2^2)D = 0$$

whence approximately,

$$\frac{p_2 - p_1}{\mu_1 - \mu_2} = \frac{rB}{2pD}. \qquad (64)$$

Introducing these relations into (60), (61), we find

$$M' = -\frac{r\sqrt{(p^2 + r^2) \cdot B \cdot N}}{2p^2 D}, \quad (65)$$

$$N' = -\frac{r\sqrt{(p^2 + r^2) \cdot B \cdot M}}{2p^2 D}.$$
 (66)

These equations indicate that the intensity of the reflected light  $(M'^2 + N'^2)$  is proportional to that of the incident, without regard to the polarization of the latter. Again, if the incident light be unpolarized (M and N equal, and without permanent phase relation), so also is the reflected light. But what is more surprising is, that if the incident light be polarized in or perpendicular to the plane of incidence, the reflected light is polarized in the opposite manner.

The intensity of reflexion may be expressed in terms of the

angle of incidence  $\phi$ , for

so that 
$$p/\sqrt{(p^2+r^2)} = \cos\phi, \quad r/\sqrt{(p^2+r^2)} = \sin\phi,$$

$$M'^2 + N'^2 = \frac{B^2 \sin^2\phi}{4D^2 \cos^4\phi} (M^2 + N^2). \qquad (67)$$

When the angle of incidence is small, the intensity is proportional to its square. And, as was to be expected, the reflexion

is proportional to B2.

The laws here arrived at are liable to modification when, as must usually happen in practice, the thickness of the plate cannot be neglected. The incident light, on its way to the twin surface, and the reflected light on its way back, is subject to a depolarizing influence, which in most cases complicates the relation between the polarizations of the light before entering and after leaving the crystal. One law, however, remains unaffected. If the light impinging upon the crystal be unpolarized, it retains this character upon arrival at the twin face. We have shown that it does not lose it in the act of reflexion, neither can it lose it in the return passage after reflexion. Hence, if the light originally incident upon the layer of crystal be unpolarized, so is the reflected light ultimately emergent from it.

If, on the other hand, the incident light be polarized, whether plane or elliptically, the character of the emergent light must depend upon the precise thickness of the crystalline layer, and will vary rapidly from one part of the spectrum to another. The simplest case that we can consider is when the polarization of the incident rays is such that one or other of  $\Theta_1$ ,  $\Theta_2$  vanish. We will suppose that it is  $\Theta_2$ ; so that after reflexion,

$$\frac{\text{Intensity of } \theta'}{\text{Intensity of } \theta''} = \frac{p^2 + r^2 + \mu_1^2}{p^2 + r^2 + \mu_2^2} \cdot \frac{\theta'^2}{\theta''^2} \\
= \frac{\mu_1^2 - \mu_1 \mu_2}{\mu_2^2 - \mu_1 \mu_2} \frac{4\mu_1^2 \mu_2^2}{\mu_1^2 (\mu_1 + \mu_2)^2} = \frac{-4\mu_1 \mu_2}{(\mu_1 + \mu_2)^2} \quad . \quad . \quad (68)$$

by (54), (55). This is the ratio of intensities that would be observed with an analyzing nicol held so as to retain in succession  $\theta'$  and  $\theta''$ . If the crystalline layer be moderately thick, and the light be of mixed wave-lengths, there will be no interference observable between  $\theta'$  and  $\theta''$ , and thus the ratio just found is the extreme ratio of intensities. By means of (62) we may express it in terms of the angle of incidence  $(\phi)$ , and of the fundamental optical constants of the crystal. Thus

$$\sqrt{\left\{\frac{-\mu_{1}\,\mu_{2}}{(\mu_{1}+\mu_{2})^{2}}\right\}} = \frac{\sqrt{\left\{p^{2}+r^{2}\right\} \cdot Br}}{(A-C)r^{2}+(D-C)p^{2}}$$

$$= \frac{B\sin\phi}{(A-C)\sin^{2}\phi+(D-C)\cos^{2}\phi}. \qquad (69)$$

This expression shows that in general the emergent light will be fully polarized only when  $\phi$  is very small. In this case we virtually fall back upon our original investigation where the thickness of the layer was neglected. Since only  $\Theta_1$  is present, there is no depolarization in the first passage; and when  $\phi=0$  there is no depolarization upon the return passage in consequence of the disappearance of  $\theta'$ . The polarizations corresponding in this case to  $\Theta_1$ ,  $\Theta_2$  are obviously those in and perpendicular to the plane of incidence; and we learn that, when the angle of incidence is small, polarizations in and perpendicular to the plane of incidence are reversed in the reflected ray. If the incident ray be polarized in other directions than these, the reflected ray is in general not fully polarized, even though the angle of incidence be small.

XXVI. On the Remarkable Phenomenon of Crystalline Reflexion described by Prof. Stokes. By LORD RAYLEIGH, Sec. R.S.\*

THE phenomenon in question is that exhibited by certain crystals of chlorate of potash, consisting of a peculiar internal coloured reflexion. The following, stated very briefly, are its leading features as described by Stokes †:—

(1) If one of the crystalline plates be turned round in its own plane, without alteration of the angle of incidence, the peculiar reflexion vanishes twice in a revolution, viz. when the plane of incidence coincides with the plane of symmetry of the crystal.

(2) As the angle of incidence is increased the reflected

light becomes brighter and rises in refrangibility.

(3) The colours are not due to absorption, the transmitted

light being strictly complementary to the reflected.

(4) The coloured light is not polarized. It is produced indifferently whether the incident light be common light or light polarized in any plane, and is seen whether the reflected light be viewed directly or through a Nicol's prism turned in any way.

(5) The spectrum of the reflected light is frequently found to consist almost entirely of a comparatively narrow band. When the angle of incidence is increased, the band moves in the direction of increasing refrangibility, and at the same time increases rapidly in width. In many cases the reflexion

appears to be almost total.

Prof. Stokes has proved that the seat of the colour is a narrow layer, about a thousandth of an inch in thickness, in the interior of the crystal; and he gives reasons for regarding this layer as a twin stratum. But the phenomenon remains a mystery. "It is certainly very extraordinary and paradoxical that light should suffer total or all but total reflexion at a transparent stratum of the very same substance, merely differing in orientation, in which the light had been travelling, and that, independently of its polarization."

From the first reading of Prof. Stokes's paper, I have been much impressed with the difficulty so clearly set forth. It seemed impossible that a combination of two surfaces merely could determine either so copious or so highly selected a reflexion. If light of a particular wave-length is almost totally reflected, what hinders the reflexion when the wave-

<sup>\*</sup> Communicated by the Author. † Proc. Roy. Soc. Feb. 1885.

length is altered, say, by one twentieth part? Such a result may arise from the interference of two streams under a relative retardation of many periods; but in that case there are necessarily a whole series of wave-lengths all equally effective. The prism should reveal a number of bright bands and not merely a single band. The selection of a particular wave-length reminds one rather of what takes place in gratings; and I was from the first inclined to attribute the colours to a periodic structure, in which the twins alternate a large number of times. Such a view explains not only the high degree of selection, but also the copiousness of the reflexion.

Partly with a view to this question, I have discussed in a recent paper \* the propagation of waves in an infinite laminated medium (where, however, the properties are supposed to vary continuously according to the harmonic law), and have shown that, however slight the variation, reflexion is ultimately total, provided the agreement be sufficiently close between the wave-length of the structure and the half wave-length of the vibration. The number of alternations of structure necessary in order to secure a practically perfect reflexion will evidently depend upon the other circumstances of the If the variation be slight, so that a single reflexion is but feeble, a large number of alternations are necessary for the full effect, and a correspondingly accurate adjustment of wave-lengths is then required. If the variation be greater, or act to better advantage, so that a single reflexion is more powerful, there is no need to multiply so greatly the number of alternations; and at the same time the demand for precision of adjustment becomes less exacting. The application of this principle to the case of an actual crystal, supposed to include a given number of alternations, presents no difficulty. At perpendicular incidence symmetry requires (and observation verifies) that the reflexion vanish: but, as the angle of incidence increases, a transition from one twin to the other becomes more and more capable of causing reflexion. Hence if the number of alternations be large, the spectrum of the reflected light is at first limited to a narrow band (whose width determines in fact the number of alternations). As the angle of incidence increases, the reflexion at the centre soon becomes sensibly total, and at the same time

<sup>\* &</sup>quot;On the Maintenance of Vibrations by Forces of Double Frequency, and on the Propagation of Waves through a Medium endowed with a Periodic Structure," Phil. Mag. Aug. 1887.

the band begins to widen \*, in consequence of the less precise adjustment of wave-lengths now necessary. At higher angles the reflexion may be sensibly total over a band of considerable width. All this agrees precisely with Prof. Stokes's description of the case considered by him to be typical. The movement of the band towards the blue end of the spectrum is to be attributed to the increasing obliquity within

the crystal, as in the ordinary theory of thin plates.

It thus appears that if we allow ourselves to invent a suitable crystalline structure, there need be no difficulty in explaining the vigour and purity of the reflexion; but such an exercise of ingenuity is of little avail unless we can at the same time render an account of the equally remarkable circumstances stated in (1) and (4). When the incidence is in the plane of symmetry, no reflexion takes place. As Prof. Stokes remarks, this might be expected as regards light polarized in the plane of symmetry; but that there should be no reflexion of the other polarized component is curious, to say the least. Not less remarkable is it that when the incidence is in the perpendicular plane, the reflected light should show no signs of polarization. The phenomenon being certainly connected with the doubly refracting property, we should naturally have expected the contrary.

The investigation of the reflexion from a twin-plane, contained in the preceding paper (pp. 246 et seqq.), shows, however, that the actually observed results are in conformity with theory. In the plane of symmetry there should be no reflexion of either polarized component, at least to the same degree of approximation as is attained in Fresnel's well-known formulæ for isotropic reflexion. As regards light reflected in the perpendicular plane, theory indicates that if the incident light be unpolarized, so also will be the reflected light. Again, the intensity of the (unanalyzed) reflected light should be independent of the polarization of the incident. So far there is complete agreement with the observations of Prof. Stokes. But there is a further peculiarity to be noticed. Theory shows that in the act of reflexion at a twin plane, the polarization is reversed. If the incident light be polarized in the

 $\delta\mu = -2B\lambda^{-3}\delta\lambda$ ; so that if the rand correspond in every position to a given relative range of  $\lambda$ , its apparent width (reckoned as proportional to  $\delta\mu$ ) will vary as  $\lambda^{-2}$ . In a diffraction-spectrum this cause of widening with diminishing  $\lambda$  would be non-existent.

<sup>\*</sup> It should be observed that if the spectrum be a prismatic one, there is a cause of widening which must be regarded as purely instrumental. According to Cauchy's law  $(\mu=A+B\lambda^{-2})$ ,

plane of incidence, the reflected light is polarized in the perpendicular plane, and vice versâ. When I first obtained this result, I thought it applicable without reservation in the actual experiment, and on trial was disappointed to find that the reflected light was nearly unpolarized, even when the incident light was fully polarized, whether in the plane of incidence or in the perpendicular plane. When, however, the angle of incidence was diminished, the expected phenomenon was observed, provided that the original polarization were in, or perpendicular to, the plane of incidence. If the original polarization were oblique, the reflected light was not fully polarized, even though the angle of incidence were small\*.

Further consideration appeared to show that the loss of polarization usually observed could be explained by the depolarizing action of the layer of crystal through which the light passes, both on its way to the reflecting plane and on its return therefrom. As is shown in the preceding paper, this depolarizing action does not occur when the angle of incidence is small, and the polarization in, or perpendicular to, the plane of incidence. It seems scarcely too much to say that the theory not only explains the laws laid down by Stokes, but also predicts a very peculiar law not before suspected.

The theory, as so far developed, is indeed limited to incidences in the two principal planes. It could probably be treated more generally without serious difficulty; but there seems no reason to suppose that anything very distinctive would emerge. It is not unlikely that the intensity would prove to be proportional to the square of the sine of the angle between the planes of incidence and of symmetry. If this theory be accepted—and I see no reason for distrusting it—the brilliant reflexion cannot be explained as due to a single twin stratum. The simplest case which we can consider is when the angle of incidence is small and the polarization in or perpendicular to the plane of incidence. There is

<sup>\*</sup> Whatever the angle of incidence, the arrangement of crossed nicols may sometimes be conveniently applied in order to isolate the light under investigation from that reflected at the front surface of the crystalline plate. In the observations described in the text the crystal was mounted with Canada balsam between thick plates of glass, so that there was no difficulty in observing separately the various reflexions. At small angles of incidence the coloured image is at its brightest when the analyzing nicol is so turned that the white image (reflected from the glass) vanishes, and vice versa, the incident light being polarized in, or perpendicularly to, the plane of incidence.

<sup>†</sup> The wording of Prof. Stokes's description is perhaps a little ambiguous, but I gather that he did not examine the result of a simultaneous operation of polarizer and analyser.

then sensibly but one wave reflected at the first twin plane. On the arrival of the transmitted wave at the hinder surface of the twin stratum, a second reflexion ensues, similar to the first, except for the reversal of phase due to the altered circumstances. The relation to one another of the two reflected waves is exactly the same as in the ordinary theory of thin plates, and does not appear to admit of the production of anything unusual. I think we may even go further, and conclude that in conformity with our theory it is impossible to find an explanation of the brilliant and highly selected reflexion, unless upon the supposition that there is a repeated alternation of structure.

The optical evidence in favour of the view that there are a large number of twin planes thus appears to be very strong; the difficulty is rather to understand how such a structure can originate. And yet if we admit, as we must, the possibility of the formation of one twin plane, and of two twin planes at a very small distance asunder\*, there seems nothing to forbid a structure regularly periodic, which may

perhaps be due to causes vibratory in their nature.

It would undoubtedly be far more satisfactory to be able to speak of the periodic structure as a matter of direct observation, and it is to be desired that some practised microscopist should turn his attention to the subject. Ex hypothesi, we could not expect to see the ruled pattern upon a section cut perpendicularly to the twin planes, as it would lie upon, or beyond, the microscopic limit. I have tried to detect it upon a surface inclined to the planes at a very small angle, but hitherto without success.

In the absence of complete evidence it is proper to treat the views here put forward with a certain reserve; but it is perhaps not premature to consider a little further what may be expected to result from a structure more or less regular. If the periodicity be nearly perfect, the bright central band in the spectrum would be accompanied by subordinate bands of inferior and decreasing brilliancy. If the angle of incidence be small, so that the aggregate reflexion is but feeble, each stratum may be considered to act independently, and the various reflected waves to be simply superposed. The resultant intensity will depend of course upon the phase relations. At the centre of the band the partial reflexions agree in phase, and the intensity is a maximum. As we leave this point in either direction, the phases begin to

<sup>\*</sup> This is the simplest supposition open to us, when, as in most of the coloured crystals, the parts on either side of a very thin lamina are similarly oriented.

separate. When the alteration of wave-length is such that the phases of the reflected waves range over a complete cycle, the resultant vanishes, and a dark band appears in the spectrum. The same thing occurs whenever the relative retardation of the extreme components amounts to a complete number of periods. At points approximately midway between these, the resultant is a maximum, but the values of the successive maxima diminish \*. Near the central band, where (when the number of alternations is great) a considerable fraction of the incident light is reflected by the system of layers, this way of regarding the matter may cease to be applicable, for then the anterior and the posterior layers act under sensibly different conditions.

Apart from the magnitude of the complete linear period, something will depend upon the manner in which it is divided between the twins. The most favourable, as it is also perhaps the most probable, arrangement is that in which the thicknesses are equal. In that case every partial reflexion may agree in phase. If the thicknesses, though regular, are unequal, we may first form the resultant for contiguous pairs, and then consider the manner in which the partial resultants

aggregate.

It will be seen that even if the thicknesses of the twins are equal, there are still two ways in which a regularly laminated crystal may vary, as compared with the single kind of variation open to a simple twin stratum. These are the magnitude of the linear period, and the number of periods. Comparison of a number of coloured crystals † seems to favour the view that there are important differences of constitution, even when the colour is the same at a given incidence.

In many cases the appearances are such as to suggest that the periodicity is imperfect. A little irregularity might alter or obliterate the subordinate bands, while leaving the central band practically unaffected. Sometimes there is evidence of two or more distinct periods, each sustained through a number of alternations. If the period were subject to a gradual change, the central band in the spectrum of the reflected light would be diffused, even at small angles of incidence. The

\* The case is similar to that of the distribution of brightness in the neighbourhood of a "principal maximum," when light of given wave-

length is diffracted by a grating.

<sup>†</sup> For a rich collection of such crystals I am indebted to Mr. Muspratt. He informs me that, though the result of a second crystallization from comparatively pure liquids, the coloured crystals are but rarely found when the chlorate is produced by the magnesium process.

mere broadening of the band might be due to fewness of alternations; but this case would be distinguished from the

other by the accompanying feebleness of illumination.

On the whole, the character of the reflected light appears to me to harmonize generally with the periodical theory. One objection, however, should be mentioned. It might be supposed that the total number of twin planes was as likely to be odd as to be even. In the former case the layers of crystal on either side of the thin lamina (which is the seat of the colour) would be of opposite orientations. In many crystals the character of the twinning is difficult of observation, but I have not noticed any instance of brilliant coloration answering to this description. So far as it goes this argument is in favour of the simple stratum theory; but, in view of our ignorance as to how the twin planes originate, it can hardly be considered decisive.

I have also examined a number of what appeared to be simply twinned crystals, kindly sent me by Mr. Stanford, of the North British Chemical Works. The light reflected from the twin plane is not easily observed on account of its feeble character, at least when, as in the experiments now referred to, the incidence is limited by the requirement that the light must enter the crystal at a face parallel to the twin plane. Using, however, the method described by Prof. Stokes (§ 13), I was enabled to separate the reflexions at the twin plane from those at the external surfaces of the crystal. A narrow slit admitted sunlight into the dark room, and was focused upon the crystal by a good achromatic object-glass\*. When the obliquely reflected light was examined with a hand magnifier, a ghost-like image corresponding to the twin plane could usually be detected. As the crystal was rotated in its own plane, this image vanished twice during the revolution.

It is worthy of notice that there is an evident difference both in the brightness and quality of the reflected light obtained from different crystals, even though apparently simply twinned. This suggests that, instead of a single twin plane, there may sometimes be in reality 3, 5, or a higher odd number of such in close juxtaposition. In other specimens, affording similar reflexions, the principal thicknesses on either side of a very thin layer are undoubtedly of the same kind, so that the number of twin planes must be even. Here, again, the reflected light exhibited marked differences, when various crystals were examined. In none of those now referred to could the light reflected from the thin layer be

observed without very special arrangements.

<sup>\*</sup> I did not succeed in my first trials when I employed a common lens.

In these experiments the light entered and left the crystal by a face parallel to the twin planes. In one specially wellformed and apparently simply twinned crystal I was able to observe a much more oblique reflexion from the internal surface or surfaces. The light here entered and left the crystal by cleavage faces making a large angle with the reflecting planes, and thus under conditions widely different from those considered hitherto, and in the latter part of the preceding theoretical discussion. Three reflected images were seen, all completely polarized (the original light being unpolarized), two in one direction and the third in the opposite direction. These images are coloured, and present tolerably discontinuous spectra, giving rise to a suspicion that the twin plane is not really single. These observations were made without special arrangements by merely examining the reflected images of a candle-flame, when the crystal was held close to the eye.

I have made many experiments on the crystallization of chlorate of potash in the hope of tracing the genesis of the coloured crystals, but without decisive results. Besides the usually small but highly coloured crystals, found by Stokes, I have obtained many larger ones in which the reflexion is feebler and less pure. These appear to be distinct from the exceedingly thin plates which at the early stage of crystallization swim about in the solution. Mounted in Canada balsam the crystals in question show colours of varying degrees of brightness and purity; and under these circumstances the effect can hardly be due to the action of the external surfaces (in contact with the balsam). The light disappears twice during the revolution of the plates in azimuth, just as in the case of the more highly coloured specimens. It seems natural to suppose that the reflexion takes place from twin surfaces relatively few in number, and perhaps less regular in disposition. Altogether the existence of these crystals favours the view that fully formed colour is due to a large number of regular alternations.

Some interesting observations bearing upon our present subject have been recorded by Mr. Madan\*. Transparent crystals, free from twinning, were heated on an iron plate to the neighbourhood of the fusion-point. During the heating no change was observable, but "when the temperature had sunk a few degrees a remarkable change spread quickly and quietly over the crystal-plate causing it to reflect light almost as brilliantly as if a film of silver had been deposited on it." Subsequently examined, the altered crystals are found to

<sup>\* &</sup>quot;On the Effect of Heat in changing the Structure of Crystals of Potassium Chlorate," 'Nature,' May 20, 1886.

"reflect little light at small angles of incidence, but at all angles greater than about 10° they reflect light with a brilliancy which shows that the reflexion must be almost total..... When the plate is turned round in its own plane, two positions are found, differing in azimuth by 180°, in which the crystal reflects no more light than an ordinary crystal under the same conditions. In these cases the plane of incidence coincides with the plane of crystallographic symmetry."

Mr. Madan worked with comparatively thick (1 millim.) plates, from which the associated twin had been removed by grinding. In repeating his experiments I found it more convenient to use thin plates, such as may be obtained without difficulty from crystallizations upon a moderate scale, and which appear to be free from twinning\*. There seems to be little doubt that the altered crystals are composed of twinned layers. Except in respect of colour, there is no difference between the behaviour of these crystals and that of the brilliantly iridescent ones described by Stokes. If light be incident at a small angle, and be polarized in or perpendicularly to the plane of incidence, the polarization of the reflected light is the opposite to that of the incident.

The only difference that I should suppose to exist between the constitution of these crystals and that of the iridescent ones is, that in the former case the alternations are irregular, and also probably more numerous. Mr. Madan conceives that there are actual cavities between the layers in the heated crystals, comparing them to films of decomposed glass †. It is, however, certain that no closeness of contact could obviate the optical discontinuity at a twin plane; and there is besides a marked experimental distinction between the cases in question. It is easy to observe, and was, I think, observed by Brewster, that the application of water to a film of decomposed glass destroys the effect. The water insinuates itself

\* It is not clear why composite crystals free from included motherliquor should suffer disruption upon heating. A line drawn on the twin plane would tend to expand equally, to whichever crystal it be considered

to belong.

<sup>† &</sup>quot;Although a large amount of light must escape reflexion at a single cavity, yet if the transmitted rays encountered a large number of precisely similar and similarly situated cavities at slightly lower levels in the crystal, the sum of the partial reflexions would produce an effect almost equivalent to a total reflexion of the original incident ray, and a corresponding deficiency in the amount of light transmitted through the whole plate. The brilliancy of the colours in the light reflected from the well-known films of decomposed glass is accounted for in precisely the same way, and the successive separate films of glass can be easily seen under a microscope at the edges of the compound film, where they only partially overlap."

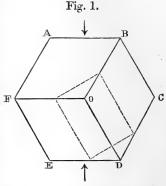
into the cavities, and greatly attenuates the reflecting power. If a corresponding experiment be tried, by wetting the edge of one of Mr. Madan's crystals with saturated solution of the

salt, no change is observed to ensue.

Whether there are cavities or no, the fact that during the preparation the silvery reflexion does not set in until the crystal has sensibly cooled is of great interest. I have found that if a crystal in which the silvery lustre has already been produced be reheated, the lustre disappears, to return again upon a fall of temperature. The operation may be repeated any number of times.

The existence of twin strata in Iceland spar was observed by Brewster\*, and Reusch† has shown that such strata can be induced artificially by suitably applied pressure (fig. 1) in

rhombs originally homogeneous. The planes of these strata truncate the polar edges, i. e. the edges which meet symmetrically at the obtuse trihedral angle (O). Being desirous of examining whether the reflexion from these strata would conform to the law deduced from theory, I submitted a rhomb to the treatment prescribed by Reusch with the effect of developing several exceedingly thin twin laminæ (four or five at least) in close juxtaposition.



When light is reflected from these strata in a plane perpendicular to the edge (O D) which they truncate, the brilliancy is considerable. But the observation which I wished to make required that the plane of incidence should be perpendicular to this, so as to include the truncated edge and the optic axis. Without much difficulty it was proved that in this plane the reflexion vanished, reviving on either side as the plane of incidence deviated a little from the plane of symmetry. The observation was facilitated by immersing the crystal in a small cell containing water or bisulphide of carbon, the twin strata being horizontal, and the plane of symmetry parallel to two of the sides of the cell.

<sup>\*</sup> Treatise on Optics, 1853, p. 349. † Pogg. Ann. t. xii. p. 448 (1867).

XXVII. On a Hydrostatic Balance. By J. Joly, M.A., B.E., Assistant to the Professor of Civil Engineering, Trinity College, Dublin\*.

[Plate II.]

THE hydrostatic balance described in this paper will be found illustrated on Plate II., reference to which will enable its principle to be the more readily understood. It will be seen from fig. 1 that it consists essentially of a vessel provided with one narrow tubular opening, and suspended so that this tubulure is downward. Within is a second vessel; this vessel is closed, and is made of such light material that it floats buoyantly in water.

A fine wire is attached to the lower end of this inner vessel, and passes through the tubulure, which is fixed onto the outer vessel by a nozzle so that, when this is screwed off, and the vessel turned up, the space surrounding the float can be readily filled with water. When filled, and the nozzle replaced, the vessel is hung up, as in the figure, with the tubulure downwards. The diameter of the tubulure being only some 3 millim., there is perfect security against outflow; indeed the apparatus may be shaken or rolled about upon a table with impunity. When the balance is hung it is obvious that the inner vessel or float, in virtue of its buoyancy, will tend to ascend within the liquid, and if, as in fig. 2, we hang a pan on the wire, and load weights on the pan, we find that we can add weights up to a certain point, when the pan descends with the sinking of the float within the vessel. weight-just adequate to cause the pan to descend-we assume for the present to be constant, and equal W, suppose, W is evidently equal to the weight of a mass of water having a volume equal to the displacement volume of the float, less the weight of the float, of the wire, and of the pan attached to the wire. We can evidently ascertain, now, the weight of any mass not heavier than W. It is as if we were using a balance, one arm of which was loaded with an unalterable weight W. Thus, we place the substance to be weighed on the pan, and add weights till the pan descends. At this point we know that the weight W is in the pan. If the added weight amounts to w, suppose, then x = W - w.

Practically, however, W is a quantity variable with the temperature of the float and of the water, their densities altering to different extents. When, therefore, accurate results are required, we cannot assume any constant for the balance, but must determine afresh the force W with each

<sup>\*</sup> Communicated by the Author.

determination of x. Or, what is the same, we proceed by simply removing x when equilibrium has been obtained with x+w, and substituting a weight  $w_1$ , so that equilibrium is again obtained, when  $w_1$  is the required value of x. It is easy to guard against change of temperature in the brief interval necessary to effect the successive equilibrations. The process of weighing is, in short, the well-known one of substitution, and with the usual correction for unequal air displacements of the weights and the substance is accurate to a degree depending on the sensibility of the float to indicate a small change of load, when the downward acting forces are very nearly in equilibrium with the upward acting forces. This consideration, *i.e.* the degree of sensitiveness possessed by the arrangement, next claims attention.

The system as described is, in principle, identical with the Nicholson hydrometer, used as a weighing machine, the latter arrangement being supposed inverted while still retaining the liquid. But the inversion of the hydrometer introduces this important difference, that the stem supporting the pan of the hydrometer, a compression member, becomes in the hydrostatic balance a tension member, and hence, stiffness being no longer a requisite, may be made of extreme fineness, and the retarding effect of the adhesion of the liquid on the wire

at its circle of emergence much reduced.

If, indeed, we assume the effect of this adhesion of the surface-film to increase in direct proportion to the radius of the circle of emergence, it would appear-observing that the tensional strength of the wire increases proportionally to the square of its radius—that the sensibility to a small fraction of the entire load falls off only as the square of the carrying capacity or load which the balance will bear. There is, in short, reason to expect that, as we increase the size and carrying capacity of this kind of balance, no diminution of the fractional sensibility occurs, but rather an increase; the sensibility increasing approximately as the square root of the power of the balance. Thus, if we double the diameter of the wire, the balance will now indeed indicate nothing smaller than double the least weight formerly causing displacement: but, on the other hand, we may assume a quadrupled carrying capacity. This leaves out of consideration the effect of viscosity of the liquid.

The effect of viscosity will hardly be to reduce the sensibility, but rather to render more tedious the use of floats having large displacements. As, however, the tangential resistance to the motion of a solid surface, in the act of communicating a shearing strain to a liquid, is proportional to

the extent of surface, and as this area increases at a slower rate than the volume inclosed by it, it appears that the tediousness attending operations is, again, not fairly assumed to be an attendant disadvantage which increases proportionally with increase of power of the balance. The effect is indeed, probably, complicated by the presence of currents or eddies in the liquid.

As regards the effects of solid friction, contact between the movable and immovable parts might, indeed, be altogether avoided. Thus we might attach the wire externally to a flat cantilever, or flat spiral-spring, so that it is retained in the centre of the tubulure by the horizontal rigidity of the spring, while the spring may possess such small vertical rigidity as not to interfere with the sensibility of the balance. It will be seen, however, from the figures, that this plan is not resorted to. It appears, indeed, unnecessary to do more than guard against contact down the wall of the tubulure; and this is provided for in the little projecting collar placed at the point where the tubulure meets the wider nozzle. The diameter of the passage here provided for the wire is about 1.5 millim.; the tubulure is about 3 millim. in diameter. The edge of the collar is sharpened to a knife-edge all round, but just burnished smooth. With this arrangement, if the precaution be taken of using a smooth piece of wire, there appears but little retardation due to friction: this, doubtless, is partly due to the position of the collar within the liquid, the liquid acting as a lubricant. The effect of substituting a collar of burnished agate for the brass collar has been tried as in the balance, fig. 2, but with hardly appreciable gain in freedom. little balance (fig. 2) is represented half its actual dimensions. The float is a sphere of thin blown glass, weighing about 12 grammes, its diameter being about 6.3 centimetres. The outer vessel is of brass, parting, in a screw-joint, into hemispheres. For convenience of weighing by replacement, a double pan of thin brass is attached to the wire. This pan, together with the suspending gear, weighs about 11 grammes. The suspending wire traversing the surface of the liquid is of brass; its diameter is 0.09 millim. Its breaking strength is 403 grammes.

The balance is protected from draughts and sudden changes of temperature by a glass case, from the roof of which it depends, hanging freely \*. The weights are introduced at a

<sup>\*</sup> For delicate work the further precaution of preserving the whole in a chamber not exposed to sudden fluctuations of temperature is, I find, necessary. Trouble from this source might be guarded against by surrounding the outer vessel with a non-conducting covering.

half door in the lower part of the case. The case needs no

levelling-screws.

At 6°C. the load carried in the pan, when equilibrium obtains, is 104.660 grammes. A change of load of 1 milligramme now causes displacement, and effects the descent or ascent of the pan. This balance then estimates the weight of

100 grammes to an accuracy of 100,000.

I must here observe, however, that working the balance to this degree of accuracy needs some care. Where estimation to an accuracy of, say, three milligrammes only is needed no special precautions are likely to be required. But with the construction shown in the figure for confining the travel of the pan and float there would seem to be an amount of adhesion before the pan is set in motion, which the small force of one milligramme will sometimes be unable to overcome. It is seen in figs. 1 and 2 that the double-eyed link to which the suspension wire is attached moves through—but without contact while moving-an eye which arrests its motion ascending and descending, affording it only about one centi-The float thus never reaches either to the top or to the bottom of the containing sphere, and adhesion at these points is avoided. The construction of this link is simple. but necessitates the exercise of a little care in the process of equilibration in order that the effect of adhesion at the link may be guarded against. Thus it may be necessary to shake the balance by tapping the case, or to bring the link to the centre of its run with the forceps, when dealing with the last couple of milligrammes. It would, doubtless, be easy to arrange, so that the adhesion necessitating these precautions when weighing with the milligrammes would be eliminated. In fig. 3 two kinds of bearing are suggested: one (a) where there is contact at two points; the other (b) at one point only, when the link is at either limit of its run.

All these arrangements secure the advantages of guarding the wire against the effects of a very excessive weight added erroneously, and of rendering a slow motion of displacement more readily observable. If care is taken in adding and removing weights, the wire remains uniformly in the one

state of strain.

If delicate weighing is to be carried out on these balances, it is necessary to use water that has been carefully filtered, as sediment will settle down into the tubulure, and clog the wire, adhering to it as it emerges from the liquid.

In the balance depicted in fig. 1 there is no provision for the effects of variation of temperature: any notable change of temperature will, with that construction, result in drawing air into the containing vessel, or expelling some of its contents. For occasional use, where the balance is filled and emptied frequently, as in travelling, this will cause no trouble as the effects of small temperature change will be inconsiderable. Thus, taking the case of concentric spheres of brass, the inner displacing 179 grammes (diam.=7 centims.), the outer having a diameter of 9 centims., and the intervening space filled with water, the effect of 1° C. change is a displacement of 14 cubic millimetres of water, about half a drop. The entry of a little air obviously does no harm: it simply rises to the top of the vessel, and in no way interferes with the truth or capacity of the machine. A little expelled water

is easily dried off.

If it be desired, however, to render the arrangement nearly permanent, so that the operation of filling need but very seldom be repeated, the effects of temperature in expelling water or drawing in air must be met in some way. In the balance of fig. 2 this is done by providing the expansion reservoir shown surrounding the tubulure, and which communicates with the interior of the sphere by the narrow tube nearly reaching to the bottom of the reservoir, as shown in the figure. The large surface of water exposed in this reservoir bears to stand at a level above or below, by a couple of millimetres, the surface level of the water in the tubulure, as in the well-known experiment on capillarity in communicating tubes of very unequal bore. Hence, with rise of temperature the reservoir receives the expelled water; with fall of temperature it parts with some of its contents, and no water is lost. The annular reservoir communicates with the air by a very small perforation, and the loss by evaporation is very small.

To enable the balance to be readily filled, the ring by which it is suspended is arranged to screw out of a little tubulure communicating with the interior. The balance is filled in a few seconds by screwing out this ring, and immersing the sphere in a vessel of water; when no more bubbles ascend through the tubulure, the ring is screwed home, while the tubulure is still beneath the surface of the water. On withdrawal a little water runs out at the lower tubulure, till the head in the reservoir has been syphoned down to a position of equilibrium with the surface-tension at the tubulure; the head is now still further reduced by applying a little bibulous paper to the tubulure, in order to provide for a subsequent

rise in temperature.

If the float be made of a substance having a low coefficient of expansion, such as glass, and the containing vessel be of material having a high coefficient of expansion, as zinc, such dimensions may be given to the apparatus that the water space will, with change of temperature, increase at the rate of expansion of water. In other words, there would be no expulsion of water or entry of air with atmospheric variations of temperature. Thus for a spherical float in a spherical chamber, and assuming any desirable radius, r, for the float, let x be required radius of outer vessel; also let g, z, w, be the coefficients of cubical expansion of glass, zinc, and water; equating the increments of volume for a rise of one degree.

$$x^3z = r^3g + (x^3 - r^3)w$$
;

q = 0.000025; z = 0.000082; w = 0.00015;  $x^3 = 1.838$   $r^3$ .

Take now the case of r=3 centims. (a displacement of 113 cubic centims.), then x=3.67 centims., which is sufficiently large, and would permit of a vertical travel of one centimetre. Such a little balance would weigh to 100 grammes and the external diameter of the outer case need not exceed 7.5

Again, the expansibilities of iron and zinc would be found With these materials the form of fig. 1 might conveniently be conferred on the balance, and large apparatus constructed, capable of carrying four or five kilogrammes, and indicating, probably, a very small fraction of the load.

The use of mercury in place of water suggests itself as a means of conferring a greater degree of compactness. In this case iron or wood might be used in their construction.

For the purpose of determining the specific gravities of solids, I use a little claw for supporting the substance under water, which can be suspended by a fine wire from a hook beneath the pan. The substance is first weighed in the pan, the claw being attached and immersed in a vessel of water placed beneath. On transferring the substance to the claw an increased weight will be required for equilibrium; the

increase is obviously the weight of displaced water.

It is observable in the hydrostatic balance that, when the float is about to descend, the system is one of unstable equilibrium. The descent of the float is accompanied, in fact, by decreased displacement in the liquid due to the emergence of the wire, the effect being similar to that of an ever-increasing downward pull upon the float: once started, it tends to descend to its lowest point. If we provide a second wire, similar to the emerging wire, extending downwards, and dipping into a vessel of water, as occurs in the operation of determining specific gravity, the effect is in all cases obviously The correction is, however, with wire of the

diameter 0.09 millim., quite unnecessary; the displacement of one centimetre of this wire representing but a small fraction,

0.06 of a milligramme.

I state these particulars at length, as I do not at present know of any other weighing machine in which a similar degree of delicacy may be so combined with the qualities of inexpensiveness and compactness, up to any ordinarily required power, as in this balance.

# XXVIII. On the Influence of Light upon Electric Discharge. By J. Borgmann.

To the Editors of the Philosophical Magazine and Journal. Gentlemen,

COME highly interesting experiments of Hertz, Hallwachs, Wiedemann-Ebert, and Arrhenius have proved irrefutably the influence of ultra-violet light-vibrations on the electric discharge of bodies in the air. Under the influence of light the potential on bodies diminishes (especially if the potential be negative); an electric current is even established between the illuminated body and any other unisolated body. ago I published two articles \*, in which I have tested the transmission of the electric current through the air in its ordinary state of elasticity and temperature. The flames or points served me in my experiments as electrodes. of such electrodes engenders a continual current through the air, even at a comparatively considerable distance between the electrodes. My experiments brought me to the conclusion that in this case one must admit on the kathode-flame considerably less particular resistance at the passage of electricity from the air to the electrode than on the anode-flame at its passage from the electrode to the air. It seems to me that there exists a link between recently made experiments, demonstrating the influence of light on the diminution of the potential upon bodies, and my own experiments. In both cases we have the formation of the electric current in the ordinary air-a fact usually not observed and even denied. In the experiments of Hertz, Arrhenius, and others the electric current in the air manifests itself in case of illuminating a negatively charged body. According to my own experiments. such a current is produced immediately between the flames or points. But if in the first case the ætherial vibrations of

<sup>\*</sup> Journal of the Russian Physico-Chemical Society, tt. xviii., xix.; La lumière électrique, xxii. pp. 193, 276, xxvii. pp. 70, 126, 182; Phil. Mag. xxiii. p. 384, xxiv. p. 374.

light falling upon the body aid the passage of the electricity from that body into the atmosphere, in my experiments such ætherial vibrations are generated by the electrode-flames themselves, or in case of electrode-points are caused by electric lights which are always formed at the extremities of the points.

Consequently, in such cases as those I mention, in the electrodes themselves are found the conditions favourable to the passage of electricity from the electrodes to the air, as is proved by the above experiments. According to all probability, on the limits separating the air from the body charged with electricity appears a particular polarization as presumed by Edlund. The ætherial vibrations of light weaken this polarization, i.e. the energy of light in this case favours the formation of the current. Something almost similar to this we have perhaps in the phenomena called photo-electric.

I repeated the experiments of Hallwachs with a zinc disk charged with negative electricity, and found that under the influence of electric light the diminution of the potential upon the disk is accomplished unequally. At the beginning of the illuminating the loss of the charge takes place much slower than afterwards, i. e. the longer the disk remains illuminated the quicker is accomplished the diminution of its potential. Some experiments even show that an after-action of the light

is observed.

I also made the following experiment:—An electric regulator was removed to a considerable distance from the zinc disk, and the electric light was weak. When the disk was illuminated no diminution of the potential on it was visible, even when a zinc screen, perforated for the passage of the light, was placed very near the disk. I removed the screen and in its stead I placed before the disk a Bunsen's flame in contact with the earth, and at such a distance that it could have no influence on the charge of the disk. As soon as the regulator was opened and the light thrown upon the disk, the diminution of the potential of the disk immediately began, i.e. a current was established between the disk and the flame. Thus the use of a flame as one electrode favorises the creation of a current through the air when a charged zinc disk standing as the opposite electrode is illuminated.

St. Petersburg, May 18, 1888. Yours truly,

Dr. J. Borgmann.

XXIX. On the Influence of a Plane of Transverse Section on the Magnetic Permeability of an Iron Bar. By Professor J. A. Ewing, F.R.S., University College, Dundee, and Mr. William Low\*.

I T has been remarked by Professor J. J. Thomson and Mr. H. F. Newall (Proc. Camb. Phil. Soc. Feb. 1887) that when an iron bar is cut across, and the ends are brought into

contact, the magnetic permeability is notably reduced.

Our attention was drawn to the matter in experimenting on the magnetization of iron in very strong fields, by what we have called the "isthmus" method †, in which a bobbin with a narrow neck was magnetized between the poles of a large electromagnet. We found that when a solid bobbin was used the central neck was much more strongly magnetized than when the neck was a distinct piece separated by planes of transverse section from the conical ends; and we were forced to ascribe the defect of permeability in the latter case to the existence of two planes of section at the ends of the short central piece of metal in which the induction was being measured. To examine the influence of transverse section more fully, and to see how far that influence is modified when the cut pieces are pressed against one another, we made a series of experiments in which the permeability of cut and uncut bars was determined by a method similar to that used by Dr. J. Hopkinson 1. The bar to be tested was let into a massive yoke of wrought iron, which provided a double path for the return of the lines of induction from end to end. effect of this is to get rid in great measure of the selfdemagnetizing influence of the bar's ends, so that the metal may be tested in a condition approximating to endlessness. Fig. 1 shows the apparatus: the bar a is sunk in holes in the yoke bb. The lower end of the bar abuts against a set screw c, and on the upper end there is an iron plunger d, through which a stress of compression can be produced in the bar by loading the lever e. The diameter of the bar was 0.79 centim. (section 0.49 square centim.); the clear length of the bar between the inside faces of the yoke was 12.7 centims., and the cross section of the yoke gave an iron surface more than 100 times greater than the cross section of the bar.

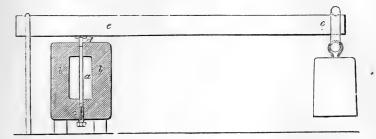
† Proc. Roy. Soc. vol. xlii. p. 200.

<sup>\*</sup> Read in abstract before Section A of the British Association at Manchester, and now published with later additions. Communicated by Professor Ewing.

<sup>‡ &</sup>quot;Magnetization of Iron," Phil. Trans. 1885, Part II. p. 455.

"magnetic resistance" of the yoke may be approximately allowed for by making a small addition to the actual length

Fig. 1.



of the bar between the faces of the yoke: in what follows this has been done by treating the bar as having a virtual length of 13 centims. The bar was wound over the whole clear length with a magnetizing solenoid through which currents were sent from a battery of accumulators. A small induction-coil less than 1 centim. long was wound at the middle of the bar, and was connected to a ballistic galvanometer, which was calibrated in the usual way by means of an earth induction-coil. To measure the magnetization the magnetizing-current was reversed several times, and readings were taken of the transient currents induced in the small coil by reversal of the magnetizing force acting on the bar. In every case a series of readings was taken, beginning with small magnetizing currents and going on to stronger ones, and from these a curve of  $\mathfrak{B}$  (the magnetic induction) and  $\mathfrak{H}$  (the magnetizing force) was drawn.

The first group of experiments show how transverse cuts reduce the permeability of a wrought-iron bar, and how longitudinal compression partially neutralizes the effect of the cuts.

The bar was turned to be of the same diameter throughout, and to fit without jamming in the holes of the yoke. It was first tested in the solid state, then when cut in the lathe into two parts, then in four parts, lastly in eight parts; in each case two curves of B and H were determined, one when the bar was not loaded, the other when it was compressed with a stress of 226 kilogs. per square centim. The results are shown by the curves of fig. 2, where the curves in full lines refer to the experiments made without load, and the dotted lines refer to those made when the bar was loaded. Comparing, in the first place, the no-load curves of fig. 2, we see

that each cutting caused a marked loss of permeability. This will also be apparent from the following table, which gives a series of values (taken from the curves) of the magnetic induction before and after cutting, for corresponding values of the magnetizing force:—

TABLE I.—Effect of Successive Cuttings.

Magnetizing force, 5	Ine	duction, B	Thickness of equiva- lent air-space, in millimetres.			
(C.G.S.units).	Solid bar.	Bar cut in two.	Bar cut in four.	For the first cut.	Mean for seven cuts.	
7·5 10 15 20 30 50 70	8500 11000 13400 14400 15350 16400 17100	6900 9000 11550 13000 14550 15950 16840	4800 6400 8900 10750 12940 15000 16120	2600 3770 5550 7150 9800 13300 15200	0·027 0·026 0·023 0·019 0·014 0·011 0·008	0·036 0·032 0·030 0·026 0·020 0·013 0·009

The last two columns of the table have been calculated on the supposition that the effect of each cut is equivalent to the introduction of a film of air, or rather of space the permeability of which is equal to unity, between the cut faces, with no alteration in the permeability of the metal itself. They show the thickness in millimetres which this equivalent air-space would need to have to explain the observed loss of permeability on the part of the bar. They are calculated by a simple application of the method introduced by Hopkinson in predetermining the magnetic field in dynamo machines\*. Calling  $\mathfrak B$  the induction before cutting and  $\mathfrak B'$  the induction for the same value of  $\mathfrak F$  after cutting,  $\mu$  the permeability of the uncut metal, l the effective length of the bar, and x the thickness of the air-space equivalent in "resistance" to the cut, the line-integral of the magnetizing force is:—

$$\frac{\mathfrak{B}l}{\mu}$$
 before cutting the bar, and  $\frac{\mathfrak{B}'l}{\mu} + \mathfrak{B}'x$  after cutting the bar;

from which

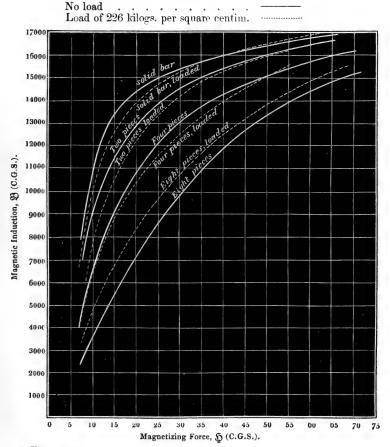
$$x = \frac{l}{\mu} \left( \frac{\mathfrak{B} - \mathfrak{B}'}{\mathfrak{B}'} \right).$$

The last column but one in the table gives values of this

<sup>\*</sup> J. and E. Hopkinson, Phil. Trans. 1886, Part I.

quantity corresponding to the first cut; the last column gives mean values for the seven cuts by which the bar was finally divided into eight pieces. It will be seen that the average thickness of air-space in the later cuts has been greater than in the first, probably because the first cut has happened to produce flatter faces than the subsequent cuts. As the magnetizing force is increased, the thickness of the equivalent air-space diminishes to a very marked degree\*.

Fig. 2.—Effects of successive cuttings on the magnetic permeability of a wrought-iron bar.



\* The magnetic "resistance" of the joint may of course also be expressed as equivalent to so much length of the iron bar itself, this length being found by multiplying the thickness of "air-space" by the permeability of the solid bar, under corresponding values of 5. The numbers in the last column, treated in this way, give from 41 to 2.2 millimetres of iron as equivalents of the resistance of the joint.

Compressive stress produced by external load has an influence of the same kind. The effects of compression are, however, complicated by the fact that this stress reduces the permeability of the solid metal (for moderate magnetizing forces\*). Hence on a cut bar it exerts two antagonistic influences, tending to increase the permeability of the bar by its action at the plane of section, and to diminish the permeability by its action on other parts; and when the planes of section are numerous enough, the former influence swamps the Fig. 2 shows that when the bar was cut into two parts the negative effect of load predominated; the dotted curve (with load) lies below the plane curve (without load). When the bar was cut into four parts, the two effects came near to neutralizing each other. When the bar was cut into eight parts the positive effect of load was the stronger; the dotted curve then lies above the plane curve. The following table gives the inductions found in the last case and in the solid bar, and the thickness of the apparent air-space at the planes of section.

Table II.—Influence of Compression (226 kilogs. per square centim.).

Magnetizing force, S.	Induction, E of 226 kilogs centin	Thickness of equivalent air-space, mean for		
	Solid bar. Bar cut in eight.		seven cuts.	
			millim.	
7.5	7500	3600	0.020	
10	10000	4900	0.019	
20	13900	8300	0.018	
30	15200	10700	0.017	
50	16500	13750	0.011	
70	17200	15700	0.007	

The influence of compression is well seen by comparing the thickness of the air-space here with its thickness for corresponding magnetizing forces, when there was no externally applied load (Table I.).

<sup>\*</sup> This effect of compression becomes reversed when the magnetization is strong: the reversal corresponds to the "Villari" reversal of the effects of longitudinal pull from positive to negative when the magnetization is sufficiently intense.

This comparison makes it clear that the reduction which occurs in the thickness of the apparent air-space as the magnetizing force is raised cannot be explained as an effect of magnetic stress in drawing the parts of the bar together.

The magnetic stress  $(\frac{\mathfrak{B}^2}{8\pi})$  in dynes) amounts to less than 4

kilogs. per square centim. when B is 10,000, and to less than 8 kilogs. per square centim. under the highest value of B reached in these experiments. Nevertheless the changes of B are associated with a reduction of the apparent air-space, which is much greater than the reduction effected by an externally applied load of 226 kilogs. per square centim. It is startling to find the apparent air-space in the loaded bar diminishing from 0.020 to 0.007 millim. as the magnetization was strengthened, when the pieces of the bar were already pressed together with a force so great that the additional force

due to magnetization was relatively insignificant.

In the foregoing experiments the bar was simply cut in the lathe, without any attempt to make the ends strictly plane. In subsequent experiments comparison was made of the permeability of a bar, rough-cut in this way, with that of a bar in which the cut faces were carefully shaped by scraping and testing against a standard Whitworth-plane. For this purpose a new bar was taken, and after being tested in the solid and again in the rough-cut state (cut into two parts), the two parts were sunk tightly in a pair of cast-iron blocks with plane surfaces about 3 inches in diameter, so that the end to be faced true was flush with the surface of the block. The faces of the blocks were carefully shaped to true planes against each other and against a Whitworth-plane, the surface of the block itself and of the bar that was held in it being worked up together. The bar's permeability was examined by taking a curve of B and S in six states:-

(1) Uncut bar; no load.

(2) Uncut bar, loaded with 226 kilogs. per square centim.

(3) Bar cut in two (at the middle). Ends as cut in lathe (rough-cut). No load.

(4) Ditto, loaded with 226 kilogs. per square centim.

(5) Surfaces faced true at the cut. No load.

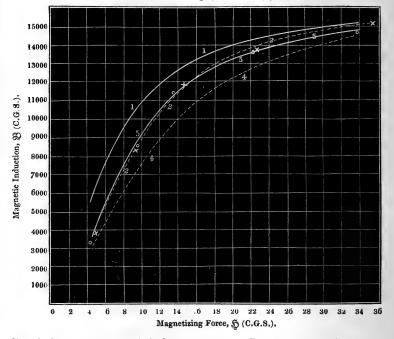
(6) Ditto, loaded with 226 kilogs. per square centim.

The results are shown in fig. 3, where four of the curves are drawn in full, and the remaining two are indicated by having the experimentally determined points marked separately. The curves are numbered to correspond with these successive operations. As in the former example, curve 2

lies decidedly below curve 1; and curve 3, which is shown only by the points marked thus O, also below curve 1; curve 4

Fig. 3.

- Solid bar, no load.
   Solid bar, loaded.
- (4) Cut bar; ends rough; loaded.
- (5) Cut bar; ends faced true; no load.
- × Cut bar; ends faced true (6).
- O Cut bar; ends rough; no load (3).



lies below curve 3 and below curve 2. But it is remarkable that curve 5 is nearly coincident with curve 3; and curve 6, which is shown only by the points marked thus ×, is almost absolutely coincident with curve 2. In other words, when the cut surfaces are faced to true planes, the cut bar does not behave very differently as regards magnetic permeability from the same bar with its cut surface only roughly shaped so long as it is not compressed by an external load. It is only when B is raised to high values that there is a marked difference; then the faced ends seem brought into better contact, and the thickness of the apparent air-space becomes decidedly less than in the case of the rough-cut bar. But when a sufficient load is applied, the cut bar with its surfaces faced true behaves

almost as a solid bar. Facing the surfaces truly does not of itself do away with the apparent air-space: so long as no load is applied the apparent space remains. But when the surfaces are faced true and the parts are strongly pressed together, the "magnetic resistance" of the joint practically vanishes.

The following table shows the induction and the thickness of the apparent air-space when the surfaces were faced to true

planes, and the bar was not loaded.

TABLE III.—Cut Bar with True-plane Surfaces.

Magnetizing	Induct	Thickness of equivalent		
force, S.	Solid bar.	Bar cut and faced.	air-space, in millimetres.	
5	6300	4300	0.058	
10	11000	9000	0.026	
15	12900	12000	0.012	
20	13900	13450	0.006	

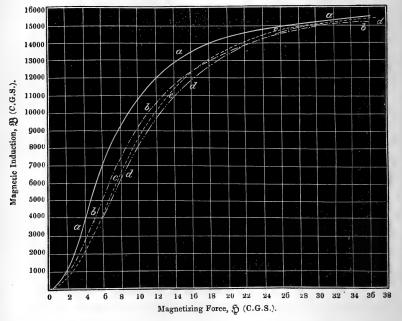
In this example the apparent air-space between the faced surfaces at the cut vanished completely under the application of load, as is shown by the way in which the points marked thus × (which refer to operation No. 6) fall very exactly on curve 2. The cut and faced bar, loaded with 226 kilogs, per square centim., could not be distinguished as to permeability from the same bar in its uncut state when that, was tested under the same load.

The above result was of so much interest, that the experiment of magnetizing a bar under load after the bar had been cut and the surfaces had been faced true was repeated on two other bars. In neither case was the apparent air-space so completely annihilated as it had been in the first instance, by the combined effect of load and true facing; but the general result was confirmed, that a bar prepared in this way and sufficiently loaded was not materially different in its magnetic properties from an uncut bar. Fig. 4 shows the results of another group of tests similar to those of fig. 3, but made with a new bar. Curve a a a is for the solid bar without load; b b b is for the same bar cut and faced, but not loaded; c c c is for the solid bar, and d d d for the cut bar, loaded in each case

with the same stress as before (226 kilogs. per square centim.). The last two curves are as nearly as possible coincident

Fig. 4.

a a a. Solid bar, no load.
b b b. Bar cut and faced, no load.
c c c. Solid bar, loaded.
d d d. Bar cut and faced, loaded.



in the early portion, and again when the magnetization is strong; at intermediate values of  $\mathfrak B$  they lie somewhat apart, the divergence corresponding to a value of about 0.0009 millim. for the maximum thickness of the apparent air-space. The divergence of the curve  $d\,d\,d$  from  $e\,e\,e$  may be due, in part at least, to some mechanical hardening of the metal in the neighbourhood of the joint by the operations of cutting and scraping (and tapping, to remove the bar from the block in which the face was scraped); the form of the curve  $d\,d\,d$  suggests this. The following figures relate to this bar in the solid state and when cut with the surfaces faced, without load:—

TABLE IV.

Magnetizing	Induc	Thickness of	
force, S.	Solid bar.	Bar cut and surface faced true.	air-space, in millimetres.
4	3950	3000	0.042
6	6900	5300	0.034
8	9250	7400	0.028
10	10900	9150	0.023
15	13250	12000	0.016
20	14300	13500	0.011
30	15200	14900	0.005

Tests made with a third bar gave results which were in close agreement with those that have just been described. In this last case comparative measurements were made of the effects of various values of external load in causing the apparent airspace between well faced surfaces to disappear. The bar, first before being cut and again after being cut, and after having its cut surfaces scraped into true planes, was magnetized under first one and then another of a series of compressing loads; the highest being of the same value as in former cases (226) kilogs, per square centim.), and a curve of  $\mathfrak{B}$  and  $\mathfrak{H}$  was found for each. As in the second example described above, this highest load did not succeed in altogether obliterating the apparent air-space except for magnetizing forces ranging up to about 5 C.G.S. units, and again for high forces. And loads less than the highest failed to make the air-space vanish, even under small magnetizing forces. To compare the effects of different loads, it will suffice to give the induction before and after cutting which was reached by applying a magnetizing force of 5 C.G.S. units to the bar, when the load had the successive values shown in Table V.

With this bar a supplementary experiment was made at the suggestion of Sir William Thomson, to examine the effect of introducing a film of gold-leaf between the (true-plane) faces of iron at the cut. It was found that when the pieces were not pressed against each other by an external load, the presence of the gold-leaf made no sensible difference in the magnetic "resistance" of the joint; when the pieces were pressed together with a force equivalent to 226 kilogs, per square centimetre, the presence of the gold-leaf did slightly

Table V.—Effects of various Loads in reducing the apparent Air-space between True-plane surfaces.

Load, kilogs. per	Induction, B, case by a mag	Thickness of equivalent air-space, in		
sq. centim.	Before cutting.	After cutting.	millimetres.	
0	5600	4700	0.022	
56.5	5400	4670	0.020	
113	4700	4200	0.017	
169.5	4050	3800	0.010	
226	3650	3650	nil.	

add to the resistance of the joint. The following table shows the induction reached under this load in the two cases, and the thickness of air-space which would be equivalent to the extra resistance which the gold-leaf apparently caused:—

Table VI.—Effect of a Film of Gold-leaf between the Faces at the Joint: Bar loaded with 226 kilogs. per square centimetre.

Magnetizing	Induct	Thickness of air equivalent		
force, S.	Without gold-leaf.	With gold- leaf.	to the differ- ence, in millimetres.	
10	8170	7920	0.0049	
20	13010	12800	0.0032	
30	14830	14720	0.0018	

The influence of the gold-leaf is therefore small, when compared with the quantities stated in the earlier tables.

The results of the experiments, taken as a whole, are very fairly consistent, but it must be admitted that they are not readily intelligible. It is not difficult to suppose that an actual film of air of such a thickness as would be required to explain the resistance of the joint may be present between the greater part of the surfaces when the surfaces are

cut in the lathe without being accurately shaped into true planes, and that this film should continue to be present when the pieces are pressed together by external load. It is less easy to see how so considerable a film of air should still be found when the surfaces are true planes, before they are pressed together. This, however, is perhaps possible enough; and the idea that the resistance is due to an actual film of air gains much probability from the fact that when truly plane surfaces are forcibly pressed together the cut bar behaves almost exactly as if it had not been cut. On the other hand. it is difficult to reconcile the idea that the "resistance" of a joint is due to an air-film, with the fact which these experiments clearly demonstrate—that the "resistance" diminishes greatly as a state of magnetic saturation is approached. We have seen that this diminution takes place under conditions which make it apparently impossible that the diminution can have been due to any real increase of closeness in the contact of the air-surfaces. In the case of a rough-cut bar strongly compressed we cannot suppose that the actual thickness of the air-space suffers any material reduction as the bar becomes magnetized. If we assume the resistance of the joint to be due to the simple presence of this air-space, the alternative would be that the permeability of air, or at least of air in the condition in which it exists when condensed on the surfaces of bodies, increases under the action of strong magnetic forces to a very notable extent, a conclusion too startling to be accepted on the evidence of these experiments alone.

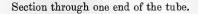
Whatever be the explanation of the results, they make it clear that a joint between two portions of the iron core of a magnet has in general a distinct magnetic "resistance," which is in all cases a function of the magnetic induction. decreasing much when the induction is increased. That this resistance is present even when the surfaces of the joint are carefully faced to be true planes; being in fact about as great then as when the surfaces are rough, if the magnetizing force is small, though less than when the surfaces are rough, if the magnetizing force is great. That when the surfaces are rough the resistance is somewhat reduced, but by no means wholly eliminated, by using force to press the parts together. when the surfaces are true planes a considerable force will destroy the resistance of the joint almost completely. And, finally, that this destruction of the resistance by pressure, when the surfaces are true planes, is only a very little less complete when a film of gold-leaf is interposed between the

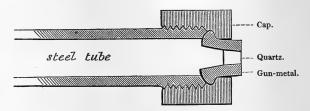
iron faces.

XXX. The Absorption-spectrum, Luminous and Ultra-violet, of large masses of Oxygen. By Professors Liveing and Dewar\*.

In the course of experiments on the spectra of gases at high pressures, we have made observations on the absorption-spectrum of oxygen which confirm and extend the observations of Egoroff and Jansen. The interest of this spectrum is so great, on account of the important part which oxygen plays in our world, and its free condition in our atmosphere, and, as we therefore conclude, in the interplanetary space, that it deserves a separate notice.

In order to include the ultra-violet rays in our observations we have had to contrive windows of quartz to the apparatus containing the gases. A strong steel tube, 165 centim. long





and 5 centim. wide, was fitted with gun-metal ends, bearing by curved surfaces upon the conical openings of the tube, and forced home by powerful screw-caps. Each gun-metal end was pierced centrally by a conical opening fitted with a quartz stopper, 2.1 centim. thick and of the same diameter, with plane polished ends. A small amount of wax was interposed between the stopper and the gun-metal for the purpose of ensuring a uniform bearing for the quartz, which is very Trial proved that the tube thus fitted would sustain, without leakage, a pressure of upwards of 260 atmospheres. The tube had, besides, near each end a screw-plug valve for admitting the gases. About the centre of the tube was placed a quartz lens, rather less in diameter than the tube, held in place by three springs which pressed against the walls of the tube. This lens had a focal length of about 46 centim.; so that when a source of light was placed about 10 centim. from one end of the tube, an image of it was formed on the slit of the spectroscope at about the same distance from the other end

<sup>\*</sup> Communicated by the Authors.

of the tube, and thereby loss of light, so far as it was due to the distance of the source, was reduced to a minimum.

Ordinary oxygen was let into the tube from an iron bottle until the pressure reached 85 atmospheres, and on viewing an arc light through the tube the following absorptions were visible:—

(1) A very dark band sharply defined on its more refrangible side, gradually fading out on its less refrangible side, and divided into two parts by a streak of light, occupying the position of A of the solar spectrum.

(2) A much weaker but precisely similar band in the

position of B of the solar spectrum.

(3) A dark band very diffuse on both edges, extending from about  $\lambda$  6360 to  $\lambda$  6225, with a maximum intensity at about  $\lambda$  6305.

(4) A still darker band a little above D, beginning with a diffuse edge at about  $\lambda 5810$ , rapidly coming to a maximum intensity at about  $\lambda 5785$ , and then gradually fading on the more refrangible side, and disappearing at about  $\lambda 5675$ .

(5) A faint narrow band in the green at about  $\lambda$  5350.

(6) A strong band in the blue, diffuse on both sides, ex-

tending from about  $\lambda 4795$  to  $\lambda 4750$ .

When photographs were taken of the ultra-violet part of the spectrum of the arc, and of the iron spark, the gas appeared to be quite transparent for violet and ultra-violet rays up to about  $\lambda$  2745. From that point the light gradually diminished, and beyond  $\lambda$  2664 appeared to be wholly absorbed.

The pressure of the oxygen in the tube was then increased to 140 atmospheres. This had the effect of increasing sensibly the darkness of all the bands above described; but brought out no new bands, except a faint band in the indigo at about  $\lambda$  4470. In the ultra-violet the absorption appeared to be

complete for all rays beyond about  $\lambda 2704$ .

The foregoing observations were made with a spectroscope of small dispersion. We next brought to bear on the spectrum a large instrument with one of Rowland's gratings. Even with the high dispersion of this instrument the bands at A could not be resolved into lines; they remained two diffuse bands; though the red potassium-lines, which were produced by sprinkling the electrode of the arc with a potassium-salt, were sharply defined and widely separated. None of the other bands were resolvable into lines. This we attribute to the density of the gas, by which the lines are expanded so as to obliterate the interspaces; and this supposition is confirmed by the observation of Angström, that the band in the solar spectrum which appears to be identical with that observed by

us a little above D was resolved into fine lines when the sun was high, but appeared as a continuous band when the sun was near the horizon.

On letting down the pressure the bands were all weakened; A, though weaker, became more sharply defined at the more refrangible edge. The faint band in the indigo  $\lambda 4470$ remained just visible until the pressure fell below 110 atmospheres. At 90 atmospheres A and B were still well seen and sharp, but all the other bands weaker. B remained visible until the pressure fell to 40 atmospheres. A was then still well seen, the band just above D very faint, and the others almost gone. At 30 atmospheres A was still easily seen, and there was a trace of the band above D. At 25 atmospheres this band had gone, but A remained visible until the pressure fell to less than 20 atmospheres. Hence an amount of oxygen not greater than that contained in a column of air 150 metres long at ordinary pressure is sufficient to produce a visible absorption at A. The quantity of oxygen in the tube at the highest pressure we used falls, however, far short of the quantity traversed by the solar rays in passing through the

atmosphere when the sun is vertical.

It will be noted that the bands, if we except the faint two in the green and indigo respectively, appear to be identical with those terrestrial bands in the solar spectrum which Angström found to be as strong when the air was dried by intense frost as at other times. At least the positions of the maxima agree closely, and that near D shows the same peculiarity in having its maximum near the less refrangible end. We did not, however, observe a, which would be fainter than B, and if, like A and B, unresolvable, would be lost in the diffuse band which covers that region. The bands above numbered 3, 4, 5, 6 agree also with those observed by Olszewski (Wied. Ann. xxxiii. p. 570) to be produced by a layer of liquid oxygen 7 millim. thick. The point also at which the absorption of the ultra-violet rays begins agrees with that at which the absorption by ozone begins, as observed by Hartley (Journ. Chem. Soc. xxxix. p. 57); but the oxygen, as we used it, did not appear to transmit the more refrangible rays beyond 2320 which seem to pass through Egoroff (Comptes Rendus, ci. p. 1144) found that A remained visible when he looked through 80 metres of atmosphere, but 3 kilog. of atmosphere failed to produce a.

When the pressure in our tube was reduced, a cloud was always formed which rendered the contents of the tube nearly opaque; the faint light which was then transmitted had

always a green tinge.

It is remarkable that the compounds of oxygen do not show any similar absorptions. Angström thought it improbable that oxygen should have a spectrum of such a character, since he failed to obtain an emission spectrum resembling it; and suggested that the absorptions might be due to carbonic-acid gas or to ozone, or possibly to oxygen in the state in which it becomes fluorescent (Spect. Norm. p. 41). Neither carbonicacid gas nor nitrous oxide, at a pressure of 50 atmospheres in our tube, show any sensible absorption in the visible spectrum; and the absorption of the ultra-violet rays by the latter gas begins at a higher point, namely about  $\lambda$  2450, than that of uncombined oxygen. In fact we see the anomalies of the selective absorption by compounds as compared with that of their elements when we take the case of water, which has a remarkable transparency for those ultra-violet rays for which oxygen is opaque.

These observations show that all stellar spectra observed in our atmosphere, irrespective of the specific ultra-violet radiation of each star, must be limited to wave-lengths not less than  $\lambda$  2700, unless we can devise means to eliminate the atmospheric absorption by observations at exceedingly high altitudes.

Postscript.—Since the foregoing paper was written we have extended our observations to much longer columns of oxygen. A steel tube 18 metres long was fitted with the same quartz ends as had been used with the shorter tube, and with two quartz lenses symmetrically placed inside the tube, one near each end, so that when an arc-lamp was placed about 14 centim. from one end of the tube the image of it was formed on the slit of the spectroscope at the same distance from the other end.

When the tube was filled with air only at ordinary pressure no absorptions could be detected, but when the air was replaced by oxygen at the pressure of the atmosphere the absorption of A was just visible, though neither B nor any other absorption-band could be traced. As the pressure of the oxygen was increased A became much darker and more distinct, and B came out sharply defined. The absorption-band about  $\lambda\,5785$  was next seen, and the dark bands about  $\lambda\,6300$  and  $\lambda\,4770$  were just visible when the pressure reached 20 atmospheres.

At a pressure of 30 atmospheres A was very black, B also strong and sharply defined, and the forementioned bands were all quite strong and had the same general characters as when seen through the shorter tube; the band about  $\lambda 5350$  also could be seen, but there was only a bare trace of that in the indigo about  $\lambda 4470$ . At 60 atmospheres these last two absorptions could be well seen, all the other bands were very strong,

B still quite sharp, but A somewhat obscured by a general absorption at the red end. At 90 atmospheres this general absorption at the red end seemed to extend to about one third of the distance between A and B; but A could still be seen, when the slit was wide, as a still darker band on a dark red background; B was still sharp, and the other absorptions all strengthened and somewhat expanded. The diffuse edges of the several bands now extended from about—(1)  $\lambda$  6410 to 6190, (2)  $\lambda$  5865 to 5635, (3)  $\lambda$  5350 to 5280, (4)  $\lambda$  4820 to 4710, (5)  $\lambda$  4480 to 4455.

Photographs taken when the pressure of the oxygen was 90 atmospheres show a faint absorption-band about L of the solar spectrum, a stronger band extending from about  $\lambda 3600$  to 3640, a broad diffuse band about the place of the solar line

O, and complete absorption above P.

The absorbent column in the tube at the highest pressure used contained a mass of oxygen about equal to that in a vertical column of the earth's atmosphere of the same section as the tube; but the intensity of the bands produced by the compressed gas was far greater than that of the corresponding bands in the solar spectrum with a low sun. When the arclight was replaced by a piece of white paper reflecting light from the sky through the tube, it appeared to the naked eye to have a faint blue tint, similar to that of liquid oxygen, which, comparing our observation with Olszewski's, seems to have the same absorptive powers as the dense gas, if we except A. This exception is probably only apparent, and due to the difficulty of observing A under the circumstances of Olszewski's experiment.

The greatly increased intensity of the absorption-bands at high pressures bears out Jansen's observation, that in this group the absorption is proportional to the product of the thickness of the absorbent stratum into the square of its density, while the absorptions to which A and B belong vary

directly as the density.

The appearance, on looking through the tube when gas at high pressure is streaming into it, is very much like that of a black and a colourless liquid, which do not mix, being stirred together, and the tube soon ceases to transmit any light. Transparency returns as the density becomes uniform. Currents produced by heating the tube at one or two points produce a similar effect, and show that such currents in the atmosphere of a star may stop all rays coming from its interior.

We hope before long to get the tube fitted with rock-salt ends and lenses, and to determine the total absorption of radiation by similar masses of oxygen, nitrogen, and hydrogen.

Cambridge, August 18, 1888.

XXXI. On the Existence of an Undulatory Movement accompanying the Electric Spark. By Ernest H. Cook, D.Sc. (Lond.), F.I.C., Merchant Venturers' School, Bristol\*.

## [Plate III.]

1. If a powdered substance be scattered over a smooth plate, and the plate held near a pair of terminals between which an electric spark is passing, the powder will arrange itself in a more or less regular series of concentric circles. The common centre of these circles (when the spark is small) appears to be a point directly under that halfway between the terminals. The general appearance presented by these curves will be apparent by a glance at the figures in the Plate which accompanies this paper. These are approximately of the same size as the original. It will be noticed that the figures roughly divide themselves into two classes—(1) those with a clear space in the middle, and (2) those with a circular space, within which the powder is apparently unaffected.

The first class are obtained by holding the plate near to the terminals, the distance varying with the energy of the spark. The cleared space is irregularly elliptical, with its major axis at right angles to the direction of the spark, and the area of the space increases as the intensity of the spark increases. The second class are formed when the distance between the spark and plate is increased until the

elliptical space ceases to make its appearance.

2. Mode of Obtaining the Curves.—The most convenient arrangement and the one which gives the best results is as follows:—An induction-coil has each of its terminals connected with a Leyden jar, and with one of the handles of a universal discharger. The plate with the powder scattered over it from a sieve is held under the points at a distance which can be varied at pleasure. The distance between the terminals, and therefore the length of the spark, can also be easily adjusted. On connecting the coil to the battery a succession of sparks of condensed electricity is obtained, and the powders will be seen to arrange themselves in the manner described. The first spark causes a distinct effect, but a continuance is necessary to bring out the regularity of the curves.

Should it be required to fix the powders in the positions

<sup>\*</sup> Communicated by the Physical Society: read June 23, 1888.

The paper was illustrated by a series of photographs: from two of these the figures in the Plate have been engraved.

which they have taken up, it is easily done by coating the plate beforehand with a thin layer of gum, and after the

experiment breathing on it.

3. Effect of Plate.—When the figures were first obtained it was surmised that they might be caused by the distribution of the electricity over the plate; that they were in fact modified Lichtenberg's figures. Experiments were therefore made with plates of various substances in different states as regards their surfaces; for example, whether polished or dull, electrified or unelectrified. The following materials have been examined:—glass; resinous cake of electrophorus (a mixture of shell-lac, resin, and Venice turpentine); ebonite; paper (glazed and unglazed); brass (lacquered and unlacquered); zinc; iron, tinned ditto, galvanized ditto; wood; paraffin; cardboard; and glazed and unglazed earthenware. Except that the rougher surfaces retard and prevent the regularity of the curves, no difference whatever could be observed as due to the substance or condition of the surface.

A piece of plate-glass or polished sheet of metal answers admirably for these experiments. The fact that the production of the curves is independent of the electrical state of the support (and therefore of the powder) justifies the statement that they are not caused by any peculiarity of electrical distribution.

4. Effect of Battery Power, Coil, and Condensation.— Experiments were made with the view of finding if variations in the number of cells, in the coil, and in the capacity of the condensers used, caused any alteration in the shape or frequency of the lines in which the powders arranged themselves. Other conditions remaining constant, the battery power employed to drive the coil was changed from ten pint bichromates to one. In no case could any difference be observed in the resulting figures produced. Afterwards the current was still further reduced until it was just sufficient to drive the coil, but so long as this was accomplished the figures remained unaffected.

Several coils were used in the course of the earlier experiments, but finally the work was confined to two. One of these was a very fine instrument by Ruhmkorff, kindly lent to me for the purpose of these experiments by Mr. Francis J. Fry, late High Sheriff of Bristol. It contains a secondary coil, formed of twenty-four miles of wire, is fitted with both spring and mercury interrupters, and with one bichromate (carbons  $7'' \times 3\frac{1}{2}''$ ), gives a regular succession of sparks six inches long. The second was a smaller instrument, by Paterson of London, fitted with a condenser of 100 sheets of 12" by 5",

and capable of giving a small spark of about  $1\frac{1}{2}$  inch long. When coupled with the Leyden jars, of course, the length of spark was much diminished. In no case with either coil was a longer spark employed than '75 inch. No change in the appearance, regularity, or shape of the figures was caused by replacing one coil by another.

The effect of a difference in condensing-power was tried by interposing more jars. Except that the vigour of the spark caused a larger area of cleared space, no alteration could be observed. This is, of course, confirmed by the fact of the different coils, possessing condensers of different areas, giving

identical results.

5. Influence of Contact-Breaker.—It might be supposed, as was done by Grove in reference to the stratifications in partial vacuo, that the intermittent character of the currents flowing in the secondary wire caused by the interruptions in the primary-coil by the contact-breaker would have some influence in producing or regulating the curves. This, however, is not the case. The shapes did not alter no matter what coil was employed, and when the mercury-break on the large coil was used in place of the spring, no alteration in the resulting curves was produced. Moreover the curves can be obtained without the use of a coil with its necessary contact-breaker at all. For this purpose it is only necessary to connect each electrode of a Wimshurst machine to one or two Leyden jars, and to allow the highly condensed spark thus obtained to act upon the powder. In fact I have been able to produce the curves in this way without employing any jars at all. With the machine, however, they are far inferior in regularity to those produced by the use of the coil. With a 17-inch plate the best results have been obtained with jars having a total area of foil of about 1500 square inches, a spark of about 3" long, and the powder 6" below spark.

6. Nature of Electrodes.—Varying the material forming the points between which the sparks were taken made no difference in the resulting shapes. Thus the same effects are

produced by using brass, iron, or carbon points.

7. Influence of the Powdered Substance.—Soon after the first results were obtained and upon trying different substances, it became evident that, although accidental irregularities occurred, yet, upon the whole, the curves were remarkably regular. It was also very soon noticed that the frequency with which they followed each other altered with an alteration of the substance of which they were composed. This induced a desire to compare by measurement the distances between each successive curve. A large number of

No. of lines

different powders were examined, and the number of lines in a certain distance counted. Several determinations were made and the mean number taken. Although every care was taken to make these measurements as accurately as possible and to avoid sources of error, yet, from the difficulties peculiar to the case, I do not wish to pledge the absolute accuracy of the numbers, but put them forward as approximate only. It first became necessary to ascertain if the fineness of the powder affected the number of lines in a certain length. This was found not to be the case. Provided the degree of fineness was such as to admit of the production of the lines with such an amount of definiteness as sufficed for their measurement, the number of lines was found to be unaltered. The following tabular statement gives the results obtained. The actual experiment was to count the number in a quarter These have been multiplied by 4, hence the regularity of the diminution of the numbers given in the first

in 1 inch	Substances examined.
88.	Silica (powdered sand).
. 80.	Magnesia alba.
68.	Chromic oxide.
64.	Antimony sulphide; baric peroxide; fluor spar; cupric oxide; red lead; lead acetate; lead oxide; antimony; sulphur; potassium hydrogen tartrate.
60.	Borax; cobaltic oxide; starch; zinc carbonate.
56.	Binoxide of manganese; baric carbonate; tricalcic phosphate; ferrous sulphide; lead chromate; mercuric oxide; binoxide of tin; nickel monoxide; lead carbonate; calcic oxide.
52.	Sodium hydrogen carbonate; potassic sulphate; potassic carbonate; mercurous chloride; carbon; calcic hydrate.
48.	Tannin; salicylic acid; rochelle salt; ammonic sulphate; baric nitrate; copper sulphate; oxalic acid; sodic chloride; succinic acid; Epsom salts.
44.	Alum,
40.	Chalk.
The figur	es (Iron filings; baric chloride; baric sulphate; benzoic
were so inde	
nite as not	to itrate; microcosmic salt; potassium chloride;
permit cour	
ing.	sulphate; ammonium nitrate; pyrogallol.

8. Effect of Mixture.—While engaged in repeating the experiments, in order to confirm the numbers, it was found that a particular sample of calcic oxide gave 48 lines to the inch instead of 56, as given in the table. Upon examining

Substances examined

the sample it was found, however, to be an old one, and to be partially converted into carbonate. It was thus a mixture of oxide and carbonate. This led to the investigation of other mixtures. It was thus proved that the number given by a mixture of two substances was intermediate between those of its constituents. The following were examined, no particular care being taken to mix in definite proportions, but the substances simply ground up together in a mortar:—

Mixture.	Nos. due to each constituent.	No. obtained.		
		Exp. 1.	2.	3.
Calcic oxide	$\{56,40\}$	48	50	48
Magnesia alba	80 }	60	64	56
Cobaltic oxide	60	64	64	66
Cobaltic oxide.  Magnesia alba.	$\left\{ egin{array}{c} 60 \\ 80 \end{array}  ight\}$	68	64	68

9. Effect on Liquids.—In order to test if the effect could be produced on the surfaces of liquids the following experiments were made:—In place of a glass plate with the powder scattered over it, there was held under the spark a shallow vessel (an ordinary porcelain evaporating dish answers very well) containing the liquid. So long as the surface was looked directly down upon, no effect could be observed; but when regarded obliquely, minute ripples were seen to be produced upon the surface. No attempt was made to measure these, but they were judged to be of about the same size as those of the powders, that is, between the limits of 88 and 40 to the inch. The following were the liquids tested in this way:—water, mercury, alcohol, ether, glycerin, and benzol.

10. Experiments with Wimshurst Machine.—It has already been stated that the curves obtained by the aid of the machine are much inferior in regularity to those given by the induction-coil; in fact, without care they cannot be produced at all. But there are some other peculiarities which deserve notice. Thus, while with every coil used and with varying battery-power it was found that magnesia alba gave 80 lines to the inch, when the machine was used the number varied in different parts of the figure from 56 to 64. There was no particular mode of variation, that is, no crowding together at a special place, &c. This irregularity in the numbers is not, however,

a general thing; for in other cases tried, the numbers did not vary among themselves and agreed with those obtained with the coils.

The common centre of the circles, instead of being, as with the coil, halfway between the terminals, seemed to be a little nearer the positive electrode than the negative. Other experiments are, however, necessary before this can be regarded as established.

In experimenting with this machine it is necessary to avoid placing the plate too near the terminals, otherwise the powder becomes electrified, and the plate also, and the resulting figures are combinations of those showing the distribution of the electricity upon the plate, and the undulatory effect discussed

in this paper.

Most of the figures obtained with the machine were caused by the spark passing between knobs. They are imperfect at the sides, in consequence of the undulatory effect being prevented from making itself felt in those directions by the solid body of the knob coming between. Thus the portion of the circles shown are at right angles to the direction of the spark. The figure can of course be obtained from sparks taken between points, but it is more difficult. It was particularly noticed in the course of these and some other experiments that, whilst substituting a knob for a point in a Wimshurst or other machine increased the length of spark obtainable, it was just the opposite with a coil; for here the spark is considerably reduced if taken between two knobs. The longest spark with a coil is obtained either between two points, or between one point and one knob or plate.

It was also noticed that under the positive electrode the powder was scattered so as to cause a space. This is some-

times, but not always, the case under the negative.

11. Production of the Cleared Space.—It will be observed that the more or less elliptical space in the middle of the figures is not present in all. It is only produced when the plate is held close up to the terminals and when the vigour of the spark is considerable. At a first glance at a figure containing the clear space, it appears that the lines are crowded together at the ends of the major axis of the ellipse. Closer examination and careful measurement will show, however, that this is not the case, for the number of lines per unit of length is the same whether measured at the ends of the major or of the minor axis. In fact the appearance is just that of concentric circles, formed of the powder, with the material composing the smaller circles swept up so as to form the irregular ellipse.

From this fact, and also that the circles can be produced without any clearing of the powder, I am led to conclude that the production of the circles is due to an entirely different cause to that producing the space, but that both are necessary

accompaniments of the disruptive discharge.

12. Discussion of Results.—When these figures were first obtained it was imagined that they were due to the sound which accompanied the spark, and in fact gave a graphical representation of the sound-waves. This view was to some extent confirmed by finding that the same substance gave the same number of waves in the same space. If this be so, however, then there ought to be no difference in the numbers obtained with different powders; for the sound of the spark produced by a coil is remarkably constant, and, if such a term can be rightly applied to it, it is of unvarying pitch. This view, however, is also disproved by the measurements; for if it be taken that the lines show the phases of the undulatory movement, then the longest distance between similar phases is that given by powdered chalk, viz.  $\frac{1}{40}$  of an inch. But the upper limit of vibration producing a sound-wave may be taken as equal to 40,000 per second, giving a length for the wave of as nearly as possible one third of an inch, a distance thirteen times greater than the longest given by these expe-It is therefore evident that the vibrations producing these curves and those producing the sound of the spark are not identical.

From the fact that the number given by a mixture is intermediate between those of its constituents, we should be led to conclude, since the density of a mixture follows the same law, that therefore this is the factor which regulates the number given by any particular substance. If this be the case, then the powders should arrange themselves in a series, with those of the highest density at the top and those of the lowest at the bottom. A glance at the tables of results will, however, show that no such order is observed. Thus we have silica giving a higher number (88) than the heavy oxides of lead (64); magnesia alba, a substance of very low specific gravity, appearing high up in the list; and tannin, also of low specific gravity, on the other hand, appearing low down. What conditions, if any, regulate the number of these lines I have hitherto been unable to determine. Before any generalization can be made it is necessary to examine a very much larger number of substances, and experiments are being conducted with this purpose. At present, indeed, I am not disposed to attach much importance to the absolute length of any one of these undulations, but rather to the great similarity of the

measurements as a whole. For although it is likely that errors may occur in some of the individual members, it is hardly possible that the whole are erroneous. It will therefore follow that undulations of a length of about one sixty-fourth of an inch (taking the mean measurement) accompany the disruptive discharge.

The photographs from which the figures in the Plate are copied were taken for me by Mr. Dunscombe, of Bristol, and were printed from the negatives without the latter being

touched in any way.

Note, June 9, 1888.—Since the above was written, I have been informed by Prof. Rücker that he has an apparatus in his possession, made by the late Dr. Guthrie, which gives somewhat similar results. This was copied from one exhibited at the Loan Exhibition of Scientific Apparatus in 1879. It consists of an elliptical dish with vertical walls. Sand is scattered over the bottom, a glass plate placed over the top, and a series of electric sparks produced at one focus of the ellipse. The sand will then be found to arrange itself in a series of circular curves around the other focus. The curves thus produced bear a striking resemblance to those exhibited in the Plate accompanying this paper, and are of course due to the same cause.

XXXII. On the Recalculation of certain Specific Heats at High Temperatures, and the Specific Heat of Water. By WILLIAM SUTHERLAND, M.A., B.Sc.\*

In the course of some work on molecular physics I was led to search for some accurate measurements of the specific heats of liquids at high temperatures, and found that, although Hirn had conducted some good experiments, his results had not been accepted on account of their disagreement with those of Regnault. Thus, while for the heat necessary to raise ether from  $0^{\circ}$  to t Hirn gives the formula

 $q = .564t + .000799t^2 - .05268t^3 + .07181t^4$ 

Regnault gives

 $q = .529 t + .000296 t^2$ .

For alcohol Hirn gives

 $q = \cdot 4229 t + \cdot 00274 t^2 - \cdot 0_4 132 t^3 + \cdot 0_7 506 t^4,$ 

while Regnault's formula is

 $q = .5475 t + .00112 t^2 + .05221 t^3$ .

The great differences between the values for the specific heats

\* Communicated by the Author.

at 0° given by these formulæ have naturally discredited Hirn's results, seeing that Regnault's values at 0° are certainly nearly correct. In the case of CS<sub>2</sub> and CCl<sub>4</sub> Hirn's results are in much better agreement with Regnault's; but the above discrepancies, as they condemned Hirn's method, condemned therefore the whole of his results.

But by recalculating the specific heats from Hirn's experimental data I have been able to bring his results at high temperatures into good agreement with Regnault's at low, and so to obtain expressions for the specific heats of ether, alcohol,

CS<sub>2</sub>, and CCl<sub>4</sub> from 0° up to 140°.

Hirn (Ann. de Chim. et de Phys. sér. 4, x.) adopted the method of cooling, but on so large a scale that he was able to avoid the difficulties usually inherent in that method. The vessel in which the liquids were heated was of about 8 litres capacity, and might be regarded as the bulb of a huge thermometer, the stem of which was 11 metres long and was filled with mercury; the pressure of the mercury-column permitted the temperature of the volatile liquids to be raised to 160°. The size of this apparatus allowed of the introduction of an efficient stirring mechanism to keep the whole mass of liquid uniform in temperature; thus the radical difficulty of the method of cooling when used on a small scale was avoided.

When the liquid in the bulb was heated, the overflow of mercury at the top of the stem enabled Hirn to measure very accurately the expansion of the liquid up to high temperatures, and gave him a connexion between the volume and temperature of the liquid at any moment in the process of cooling. In this way he succeeded in measuring the rate of cooling at

temperatures ranging from 160° to 40°.

Unfortunately he adopted a cumbersome and inaccurate method of treating his experimental numbers in order to obtain from them the specific heats. Instead of estimating the rate of cooling direct from the experimental numbers, he found an empirical formula connecting the observed times and temperatures, and then from this, by differentiation, got the rate of change of temperature. But it is obvious that this method becomes dangerous at low temperatures; for then the rate of change becomes slow, and inaccuracy in the formula which may not appear of appreciable importance in affecting the absolute value of the temperature at a given time, may seriously affect the value of the rate of change. In other words, if the ordinate of a curve is approaching a stationary value, a formula may represent the absolute values of the ordinates fairly well and yet give large errors in the values of the small slope of the tangent.

Although Hirn's formulæ represent his experiments excellently, yet they introduce in this manner a certain amount of inaccuracy into his final determinations of the specific heats. However, it is easy to calculate from his full published data the correct values.

The cooling of the large bulb is due to two causes—(1) radiation, and (2) introduction of cool liquid from the stem. As it is the rate of cooling due to radiation only that is required in the method of cooling, we must calculate this from the

actual rate of cooling.

If, in time dt, a mass dp passes from the stem where its temperature is i to the bulb where it is  $\theta$ , then if k is the specific heat at  $\theta$ , and k' is the mean specific heat between i and  $\theta$ , the cooling effect produced by dp on the mass p in the bulb is

 $dp k'(\theta-i)/kp$ .

If, then,  $d\theta$  is the actual amount of cooling, and dr the amount due to radiation in time dt, we have

$$\frac{d\theta}{dt} = \frac{dr}{dt} + \frac{dp}{dt} \frac{k'(\theta - i)}{kp}.$$

Now dp/dt is given by Hirn in his experiments on the rate of expansion, so also is p; k'/k can be estimated with sufficient accuracy from Regnault's formula for lower temperatures; i can be taken as the temperature of the surrounding air, though that is too low; but the whole of the last term is small compared to the others, so that roughness in its estimation does not produce much effect in the first calculation of specific heats.

From the above equation, then, we get the required rate of

cooling due to radiation only.

Let P be the water-equivalent of the bulb and stirrer; then if the rate of cooling of water at temperature  $\theta$ , of specific heat  $k_1$ , is  $v_1$ , while  $p_1$  is the mass of water in the bulb, then, by the usual equation for the method of cooling, we have

$$(pk+P)v = (p_1k_1+P)v_1,$$

where v stands for dr/dt; v and  $v_1$  are calculated from Hirn's data, as explained above;  $p, p_1$ , and P are given by Hirn; whence we can calculate k if we take the values of k' from Regnault's determinations. A communication by Velten (Wied. Ann. xxi. 1884) would seem to show that Regnault's values for the specific heat of water at high temperatures are altogether worthless; but I shall show, in an addendum to this paper, that the apparent discrepancies in Regnault's

published numbers can be clearly traced to an error of copying, which, however, has had no effect on the original calculations, so that the values of the specific heat at different

temperatures have been found correctly.

The actual rates of cooling at different temperatures were obtained from Hirn's data by dividing change of temperature by time elapsed during change and taking this as the rate of cooling at the mean of the extreme temperatures. The actual rates thus found were plotted and a curve drawn amongst the points. From the curve were then taken for use in the formula the values of v for  $140^{\circ}$ ,  $120^{\circ}$ ,  $100^{\circ}$ , and  $80^{\circ}$ . As the curves lay very steadily amongst the points down to  $80^{\circ}$  and not so well below that, it seemed advisable not to use Hirn's results below that temperature, but to adopt Regnault's data at lower temperatures.

The following table contains in the first row for each substance the actual rates of cooling; in the second the rates due to radiation only in degrees per minute; and in the third the

specific heats.

Substance.	140°.	120°.	100°.	80°.
Water {	•775	·575	·410	·270
	•703	·535	·391	·264
	1·023	1·018	1·013	1·009
Ether {		1·275 1·008 ·803	·892 ·765 ·736	•580 •528 •690
Alcohol {	1·22	·92	·70	·495
	·959	·781	·626	·459
	·987	·909	·797	·712
$ ext{CS}_2 \dots  ext{}$	2·225	1·625	1·15	·761
	1·86	1·424	1·05	·715
	·284	·276	·268	·260
CCl <sub>4</sub>	2·12	1·57	1·11	·74
	1·756	1·361	·998	·685
	·243	·233	·228	·219

To obtain the most accurate values of the specific heats of these liquids at 0°, I applied the method of least squares to Regnault's experiments by the ordinary calorimeter method, and combined the results with the above to obtain the following values of the constants in the formula  $dq/d\theta = a + b\theta + c\theta^2$ , where  $\theta$  represents temperature C.

	a.	b.	·C.
Ether	• 5195	.03887	04123
CS <sub>2</sub>	•229	·0 <sub>3</sub> 391	
CCl <sub>4</sub>	·198	03136	·0 <sub>5</sub> 133

The numbers calculated for alcohol do not join on in a continuous manner with those obtained from Regnault's experiments, so that a single formula of the above type is not competent to represent both series.

Regnault's formula has been given at the beginning of this paper, and may be considered to hold from  $-10^{\circ}$  to  $50^{\circ}$ ; the numbers tabulated above give for the specific heat of alcohol from  $80^{\circ}$  to  $140^{\circ}$  the formula

$$dq/d\theta = .445 + .0026 \theta + .0592 \theta^{2}$$
.

If the two series of values given by these formulæ are to join on to one another in a continuous manner, there must be a point of inflexion between 50° and 80° in the curve which represents the relation of specific heat to temperature.

Now it is a noteworthy fact that Regnault, in his experiments on the total heats of different liquids (that is, the amounts of heat necessary to raise unit mass from 0° to t and evaporate it at t) found that alcohol was the only exceptional liquid giving a point of inflexion between 70° and 80° in the curve representing the relation of total heat to temperature. The agreement between the position of this point and of that on the specific-heat curve is suggestive of some interesting points in the molecular structure of ethylic alcohol. It would be worth while for some experimenter to determine by actual experiment how the specific heat of alcohol does vary between 50° and 80°.

## Addendum.—On Regnault's Determinations of the Specific Heat of Water at temperatures above 100°.

It is a rather remarkable fact in the history of Physics that such complete uncertainty should reign to-day as to the specific heat of water, the standard substance in calorimetry, and a fundamental quantity in the science of energy. Observer after observer has devoted himself to the question with every appearance of the most thorough provision for refined accuracy; but seems only to have made "confusion worse confounded." The latest research of any elaborateness is that of Velten previously mentioned. He draws attention to apparently great errors in Regnault's calculations of the specific heat of water from his data, giving a table in which are compared the values given by Regnault and those calculated correctly by himself from Regnault's data. In twenty-seven of the experiments the two sets of values agree well enough; but in the remaining thirteen, while Regnault's results are all greater than unity, those of Velten are all less than unity, the difference between the corresponding values in the two series amounting in one case to nearly four per cent. As the errors could not be ascribed to misprints, Prof. Wüllner wrote to the Paris Academy of Sciences to ask if any explanation could be given for them; but that body appeared to be able to furnish none.

Yet the explanation is simple enough. Regnault, in preparing his table (Mém. de l'Acad. xxi.), has, in the thirteen cases, merely copied a wrong series of numbers into the column headed "weight of hot water." I shall be able to show this quite clearly, and to prove that in his calculations he must have used the correct series of numbers. Velten, using Regnault's erroneously tabulated series, necessarily obtains erroneous results in the thirteen cases.

Regnault employed a large calorimeter with a narrow graduated neck. Its capacity, when filled to the zero-mark on the neck, was carefully determined and, with the waterequivalent of the calorimeter, was tabulated for temperatures between 10° and 30°. The neck was also calibrated, so that the water-equivalent of the calorimeter, when filled to any mark on the neck, could be determined with great accuracy. Let  $P_0$  be the water-equivalent of the calorimeter and the water at  $t_0$  which fills it to the graduation  $n_0$  on the neck. A weight, p, was then withdrawn and determined by weighing. The hot water at T was then introduced, so that the calorimeter was filled to the graduation n; the water-equivalent at the resulting temperature t of the calorimeter and its contents was then obtainable from the table; let it be P, then the weight of hot water introduced was  $P-(P_0-p)$ . Let x be the mean specific heat between T and t, supposing that between t and  $t_0$  to be unity, then

$$x(P-P_0+p)(T-t) = (P_0-p)(t-t_0).$$

But at high temperatures the high-pressure steam projected the hot water with such violence into the calorimeter that it was difficult to regulate the amount of hot water so that the free surface of the water in the calorimeter should be within the graduated neck; Regnault, therefore, had to modify his method slightly. He admitted enough hot water not to raise the surface into the graduated part of the neck; but then added enough of the cold water which he had withdrawn to bring the level of the water amongst the graduations. This small weight of water never exceeded 100 grammes; let it be denoted by  $\pi$ , then the equation becomes

$$x(P-P_0+p-\pi)(T-t) = (P_0-p+\pi)(t-t_0).$$

Thus Regnault conducted two series of experiments by slightly different methods; but he includes all his results in a single table without giving any information as to which belongs to which series. It is easy to see, however, that the second method was used in precisely the thirteen experiments in which the differences occur, namely, those numbered 3, 11, 12, 13, 27, 29, 34 to 40, the last seven corresponding to the highest temperatures; because, while in all the other experiments the quantity of hot water ranges from 9904.4 gr. to 10075.9 gr., in these it is, in all cases except one, more than 10100 gr. But according to Regnault's description of his second method, he uses less hot water in these experiments than in the others; hence we must admit that in copying the results of his second method into their appropriate places in the table of results of the first method, Regnault must have transferred a wrong series into the column headed "weight of hot water;" probably he copied his values of  $p-\pi$  instead of  $P-P_0+p-\pi$ , the true weight of hot water. At all events it will now be shown that he must have used the correct series of numbers in calculating the values of the specific heat.

For if we assume that in these thirteen experiments the level of the water in the calorimeter at t always stood at the zero mark of the neck, we can estimate from Regnault's table the quantity of water P minus the small quantity contained in n divisions of the neck. Subtracting the weight of cold water  $P_0 - p + \pi$  given by Regnault, we get the weight of hot water added minus the small quantity contained in n divisions of the neck. If we substitute this for  $P - P_0 + p - \pi$  in the above equation we shall get values of x a little too large; if then the values for the specific heat given in these thirteen cases by Regnault are a little smaller than our calculated values, we can allow that he has calculated his values from the

correct data, especially as they agree with his values in the

twenty-seven other experiments.

I have applied this test to the thirteen experiments, and find that it is satisfied in all in the manner illustrated by the following six examples. The last column but one contains the values of x as found approximately.

No. of experiment.				Specific Heat.		
	t <sub>0</sub> .	t.	Regnault.	Approximate.	Velten.	
35. 36. 37. 38. 39.	183 to 190	13 to 13·6	28 to { 29	1·01430 1·01499 1·01756 1·01487 1·01621 1·01528	1·017 1·019 1·019 1·019 1·020 1·020	·9748 ·9749 ·9798 ·9804 ·9757 ·9799

It is thus seen that Regnault's experiments are still reliable and remain the most valuable which we possess on the subject of the variation of the specific heat of water with temperature. Velten considers that his values calculated from Regnault's data confirm a formula which he has given for the specific heat of water deduced from experiments below 100°, and which makes the specific heat of water above 100° less than unity; but we see from the above that his formula is quite out of harmony with Regnault's experiments.

Rankine ('Transactions of the Royal Society of Edinburgh,' xx.) has pointed out a correction which is required in Regnault's equation to allow for the kinetic energy of the hot water projected into the calorimeter by the high-pressure steam; but it is perhaps hardly necessary to apply it till greater precision is attained in the calorimetric

measurements.

It would not have been worth while treating the matter at such length were it not for the large amount of experimental work that has already been spent on the subject and the importance of showing that the experiments of so skilled a physicist are not lost as they appeared to be, and of removing an unmerited reproach from so respected a name.

Melbourne, May 25, 1888.

## XXXIII. Notices respecting New Books.

A Treatise on Hydrodynamics, with numerous Examples. By A. B. BASSET, M.A., of Lincoln's Inn, Barrister-at-Law; Fellow of the Cambridge Philosophical Society, and formerly Scholar of Trinity College, Cambridge. Vol. I. Cambridge: Deighton, Bell, and Co. London: George Bell and Sons. 1888.

DURING the last nine or ten years, since the appearance of Lamb's 'Treatise on the Motion of Fluids,' so much progress has been made in this fascinating subject of Hydrodynamics, and so many new problems of interest have been attacked, that the appearance of the present treatise is very welcome, containing, as it does, the results of the most important investigations in the mathematical theory of Hydrodynamics which have been made in modern times, carefully brought down to date as closely as possible.

The subject is a difficult one, and taxes to the utmost the analytical resources of the mathematician; and so we find this treatise bristling with formulas involving all the functions yet invented; not only the algebraical and circular functions of the ordinary elementary text-books, but also the hyperbolic, elliptic, spherical, spheroidal, conical, and cylindrical functions of Gudermann, Abel, Jacobi, Weierstrass, Legendre, Lamé, Bessel, Mehler, and others.

To read such a treatise with profit the student must have gone through a thorough course of pure mathematics on these advanced functions. We fear that such students are becoming rarer, now that the course of mathematical subjects at Cambridge has been so much curtailed of late for the examination in mathematical honours, and that so few are encouraged to proceed to the study of the

higher subjects.

It is the fashion at present to decry collections of examples as undignified in an advanced textbook of mathematics; but to the properly trained student, examples and problems are a source of instruction and delectation, and by their introduction the book can be considerably condensed; the prolixity of foreign mathematical treatises is thus avoided, and foreign writers are now beginning to perceive this and to take a leaf out of our book by themselves introducing collections of illustrative examples, generally appropriated

from our examination-papers.

While the theory of Hydrostatics dates back to the time of Archimedes, the scientific treatment of Hydrodynamics, or the Motion of Fluids, arose only two or three hundred years ago, from the hydraulic requirements of Italian gardening and ornamental waterworks, by which Torricelli and Bernoulli were led to the discovery of the theorems bearing their names. So far as the flow of liquids in pipes or channels is controlled by fluid friction, their investigation under the name of Hydraulics is important from the practical engineering point of view; and numerous treatises exist in French and German, the most modern and complete in

our language being Prof. Unwin's article in the 'Encyclopædia Britannica.'

But Mr. Basset puts off the consideration of viscosity and fluid friction to a second volume, and contents himself for the present

with the motion of the so-called perfect fluid.

The general equations of motion are due originally to Euler and Lagrange; but these equations have undergone considerable development at the hands of Stokes, Helmholtz, and Clebsch, in their discussion of the distinction between *irrotational* and *rotational* motion; the physical and geometrical interpretation receiving also great benefit from Sir W. Thomson's investigations.

The character of the motion set up in a liquid by the motion of a solid body through it receives careful treatment in this book, and the author has exhausted all possible means of discovering new cases by the employment of electric and magnetic analogies; but as the matter stands at present, the only bodies for which the problem can be considered solved are the sphere, bodies made up of parts of a sphere, and the ellipsoid.

To George Green is due the credit of the solution (in 1833) for the case of the motion of translation of the ellipsoid, while lately Mr. W. M. Hicks has extended the case of two spheres as far as

modern analysis will allow.

The curious cases of plane discontinuous motion discovered by Helmholtz and Kirchhoff are discussed in chapter vi.; and in this direction the subject should yield some interesting develop-

ments to the investigator.

The splendid modern dynamical principle of the "ignoration of coordinates," due to Dr. Routh, enables us to apply the Lagrangian and Hamiltonian equations to the motion of a solid through liquid, and chapters viii., ix., x., and xi. are occupied with the application of these principles to all the interesting problems yet discussed.

A second volume is promised containing the theory of circular vortices, on the lines of Prof. J. J. Thomson's essay; on the motion of a liquid ellipsoid under its own attraction, including the most recent work of Poincaré and G. H. Darwin, in addition to Riemann and Dirichlet; a chapter on liquid waves and tides; and concluding with the theoretical investigation of the effect of viscosity, a subject in which the author himself has made valuable researches.

The author shirks no mathematical difficulties, and his work should prove stimulating to the pure mathematician in directing his attention to parts of analysis requiring development, as well as to the student of physical science and applied mathematics.

A. G. GREENHILL.

Sunlight. By H. P. Malet. (8vo, pp. i-xii and 1-180.) Trübner & Co.: London.

By way of enabling our readers to form some notion of this book of extraordinary views, which it would be of little use to criticize

in a systematic manner, we make the following quotation from

Mr. Malet's preface:—

"A book full of this tentative science might be written, but enough has been said to show the confusion of present schooling. The one word missing is Light; its results on gases or on their products is therefore wanting. The persistent or fickle forces of wind and water flow from the action of light; they leave the productions of ocean and of dry land along our shores. All the plateaus of our present continents are built from these products by these actions, resulting in more land by a longer light in the northern hemisphere. In these buildings gases and combustibles with their heating chemical causes are buried; from these burials we get volcanic eruptions; and from the sapping of these burials at varied depths by fire and water we get our earthquakes. The similarity of volcanic action is due to the burials being chiefly of similar materials, but the late earth actions in New Zealand tell of different constituents. In whichever way we look at these actions and materials, there is no difficulty in tracing all to Light, acting on matter sensitive to it: that matter absorbed sunlight to maintain its own light of life; caskets of earth material retained that light and give it back as fire from those materials. The whole process tells of a God of Light, of a creation by the Light of Life. this light we get our expansion of gases as evaporation; on this follows the condensation and fall of the liquid gases as they meet the colder air; then follows the rarefaction of our air by cold pressure, getting rid of all earthy particles till the upper air meets the impalpable cold ether of space without friction. From these pressed-out earthy particles Laplace thought our meteors came, a much more likely theory than from comets, as Professor Newton taught the American Association for the Advancement of Science in August last."

Having thus presented some of the writer's facts and views in his own words, we confidently leave this book to the judgment of

the reader.

Companion to the Weekly Problem-papers. By the Rev. J. J. MILNE, M.A. Macmillan. 1888.

The titlepage further sets forth that this work is "intended for the use of students preparing for Mathematical Scholarships, and for the junior members of the Universities who are reading for Mathematical Honours." Even now it is possible for a reader of the title to be totally unaware of the contents of the useful book before us.

We first glance at the headings. The theory of Maximum and Minimum is handled by the Editor under the heads of Algebraical and Geometrical, and many valuable results are arrived at in the course of the 43 pages given to it. The same gentleman also discusses the theory of Envelopes under the same two heads, with illustrations, and there is a Note appended by Mr. R. F. Davis. This last writer follows with a Note on "'Centroid' applied to Geometry;" and Prof. Genese adds one on "Force applied to

Geometry." Prof. Genese then devotes a chapter to "Biangular Coordinates:" i. e. take a triangle PAB,  $\angle PAB = \theta$ ,  $\angle PBA = \phi$ ;  $\theta$ ,  $\phi$  are the coordinates of P. Several neat results are obtained; the method, however, does not seem likely to be of general utility.

Pages 99-184 are devoted to a very full and interesting account by the Rev. T. C. Simmons, of what has been called the "Recent Geometry of the Triangle." There is nowhere to be found such a handy account, so that we can recommend those of our readers who want to know what it is all about to read this article. If, further, they procure Dr. Casey's 'Conics,' and the fourth edition of his 'Sequel to Euclid,' they will be able to learn all, or nearly all, that has been printed on the subject in English. The writer has treated the question in an independent manner, and has contributed much of novelty to it. Some of our old "Diary" friends would have revelled in this portion of the geometrical field: some, indeed, did a little in this direction, before Brocard laid his hands upon his points, and his circle, and compelled more close study of these matters. There is a short historical Note founded upon a communication by M. E. Lemoine: some corrections upon the early history of the subject are being supplied by Dr. Emmerich to the columns of the 'Educational Times' (see July 1888). Chapter vi. has four proofs of Feuerbach's theorem, by Feuerbach himself, Messrs. Davis, Langley, and Genese. The last has given, perhaps, a simpler proof still in a Note read before the London Mathematical Society at its March meeting. Chapter vii., by Mr. Langley, treats of the "Theory of Inversion" and "Pedals." The remaining chapters contain "Geometrical and Mechanical Constructions," "Theory of Elimination," "Summation of Series," "Binomial Series," and "Algebraical and Trigonometrical Identities," "Miscellaneous Articles," and specimens of recent scholarship-papers. much useful matter furnished for junior students which they will find it difficult to come across elsewhere, for the matters treated of do not come into the ordinary text-books.

A Treatise on Plane Trigonometry, containing an account of Hyperbolic Functions, with numerous examples. By J. Casex, LL.D., F.R.S. Dublin: Hodges. 1888.

The theme of the treatise before us is now a somewhat hackneyed one as it is presented in the numerous manuals which follow one another in rapid succession; but Dr. Casey, with a master's touch, has imparted a wonderful amount of freshness to the details he has grouped together. He has not only brought out of his treasure-house things new and old, but he has deftly clothed each small or great detail, and assigned it a niche which seems to be the fittest for it. He does not follow on the lines suggested by Hoüel, in his Remarques sur l'enseignement de la Trigonometrie, and run-a-muck against tedious calculations\*, but he explains at some length, and

\* "Au lieu d'occuper durant tant de mortelles heures les pauvres écoliers à transcrire de nombres à sept figures (le nombre sept est, paraît-il,

with great rigour of proof, the theorems and processes which enable computers to draw up these same seven-figure logarithmic tables, leaving the teacher to adopt Houel's suggestions or not. One thing our author commends, though he does not yet adopt the practice, and that is the use-gradually coming into vogue amongst continental mathematicians—of the logarithms of the Natural Series, &c., in place of the so-called Tabular Logarithms. Several French treatises, in addition to the English one by Hymers (Dr. Casey does not recognize apparently as independent treatises in English any of the more modern works), as well as numerous papers in mathematical journals and college examination-papers, have been drawn upon with the happiest results. The outcome is a work admirably adapted for students. For the use of Physical students especially the author, though he has been anticipated here, gives a good systematic account of the Hyperbolic and other functions, which "from their great analogy to circular functions are very interesting, and of great and increasing importance in Mathematical Physics." The generality of English students, we believe, will come across much that will be new to them in these pages, and need not fear to find a dish of the crambe repetita.

## XXXIV. Proceedings of Learned Societies.

GEOLOGICAL SOCIETY.

[Continued from p. 238.]

June 20, 1888.—W. T. Blanford, LL.D., F.R.S., President, in the Chair.

THE following communications were read:—
1. "On the Occurrence of Marine Fossils in the Coal-Measures of Fife." By Jas. W. Kirkby, Esq.

2. "Directions of Ice-flow in the North of Ireland, as determined by the observations of the Geological Survey." By J. R. Kilroe, Esq.

While the striæ S.E. of a line drawn from Strangford Lough to Galway Bay all trend in one direction, two sets of striæ occur N.W.

un nombre sacré en mathématiques comme ailleurs), et de noyer leurs idées dans les flots de chiffres, ne serait-il pas mieux de faire plus souvent appel à leur intelligence et à leur bon sens, et de leur montrer que l'art du calcul, loin d'être une routine aveugle et abrutissante, fournit, au contraire, au calculateur des occasions continuelles de développer les ressources de son esprit d'invention, en lui offrant des sujets d'expériences aussi variés qu'intéressants, et donnant lieu à l'emploi de procédés plus ou moins exacts, plus ou moins expéditifs? Loin delà, dans les Traités même les plus en vogue, on ne trouve pas un seul mot pour avertir l'écolier que l'on perd absolument son temps en prenant avec sept figures le logarithme d'un nombre connu seulement à un centième ou un millième près de sa valeur, et qu'il est insensé de conserver dans une addition plus de chiffres dans une partie des termes qu'il n'en existe dans le terme qui en a le moins."

of that line, which are generally at right angles to each other, and are frequently seen upon the same rock-surface. The direction of one of these is N. by W. in Antrim and Londonderry; N.W. over the highlands of Fermanagh; and N.E., N., and N. by W. in Donegal &c. That of the second set is W. 25° S., swinging round to W. in Donegal and S.W. towards Galway Bay, and is strikingly persistent throughout. Besides these, a very few striations occur which do not conform to these directions, and are attributable to local ice-flows.

The second set of striations was referred to the ice of the Scottish Glacial System, and evidence was cited from the researches of Messrs. Symes and McHenry, Dr. Geikie, and others in support of this view, which is confirmed by the relative positions of the boulders and their parent rocks. Strike bearing westward have been observed at a height of 1100 feet in co. Mayo.

The effects of the *Irish Glacial System* have been considered by the Rev. W. Close, Mr. G. H. Kinahan, and Prof. Hull. Striations occur up to 1340 feet in Donegal. The ice of this system flowed

in a general S.E. direction to the S. of the axis.

With regard to the relative age of the two sets of striæ, it is observable that those bearing northward are by far the most numerous; so that although it is reasonable to suppose that a considerable accumulation of snow and ice obtained in the Irish area whilst the Scotch system was gathering its maximum strength, the striations produced by this gathering would be largely effaced by the westward-flowing Scotch ice; and that, after the decline of the latter, an independent Irish Mer de glace flowed northward and southward, finding its axis of movement in the great central snow-field.

3. "Evidence of Ice-Action in Carboniferous Times." By John Spencer, Esq., F.G.S.

The author combated the notion that there is any à priori improbability in the action of ice during the period in question. In the case under consideration, of the two agents, land-ice or floating-ice, he was inclined to adopt the latter, as having been the cause of the phenomena he described. The bed affected is the Haslingden Flag-rock, a member of the Millstone-Grit series, which is directly covered by a shale of the same series. The surface of this Flag-rock is largely striated, the striæ having a N.E. and S.W. direction, and being nearly parallel. The area exposed is 200 square feet. The Flag-rock dips to the east at an angle of 30°; but there seems no possibility of these striæ having been produced by landslips or local disturbance. A quarry on the same horizon, near Rochdale, exhibits similar phenomena. As collateral evidence of ice-action, he alluded to the boulders frequently found in the coal-seams.

4. "The Greensand Bed at the Base of the Thanet Sand." By Miss Margaret I. Gardiner, Bathurst Student, Newnham College, Cambridge.

This bed may be seen between Pegwell Bay on the east, and Chislehurst on the west, and a somewhat similar bed occurs at Sudbury, Suffolk. An examination of the Kentish layer showed it to consist of 45 per cent. of quartz, 15 per cent. of glauconite, and 40 per cent. of flint. Amongst the rarer minerals are felspar, magnetite, spinel, zircon, garnet, rutile, tourmaline, actinolite, epidote, and chalcedony; and there are a few microscopic organisms, either Radiolarians or Diatoms, and some Foraminiferal casts.

The Sudbury greensand has 75 per cent. of its grains consisting of glauconite, and of the quartz- and flint-grains only 10 per cent. are flint; several of the rarer minerals found in Kent occur here

also

The large flint-percentage in the Kentish grains was alluded to in support of the existence of an unconformity at the base of the Tertiary deposits of that area; and the relatively small percentage of flint in the sands now being formed along a very similarly situated shore, was suggested to be due to the drifting of débris derived from the coasts composed of Tertiary and Wealden rocks, which became mixed with the material brought down by the Thames.

- 5. "On the Occurrence of Elephas meridionalis at Dewlish, Dorset." By the Rev. O. Fisher, M.A., F.G.S.
- 6. "On Perlitic Felsites, probably of Archæan age, from the flanks of the Herefordshire Beacon, and on the possible Origin of some Epidosites." By Frank Rutley, Esq., F.G.S.

The author has previously described a rock from this locality in which faint indications of a perlitic structure were discernible. In the present paper additional instances were enumerated and a description was given. The perlitic structure is difficult to recognize, owing to subsequent alteration of the rock.

Decomposition-products, apparently chiefly epidote, with possibly a little kaolin, have been found in great part within the minute

fissures and perlitic cracks.

The author suggested, from his observations, that felsites, resulting from the devitrification of obsidian, quartz-felsites, aplites, &c., may, by the decomposition of the felspathic constituents, pass, in the first instance, into rocks composed essentially of quartz and kaolin; and that by subsequent alteration of the kaolin by the action of water charged with bicarbonate of lime and more or less carbonate of iron in solution, these may eventually be converted into epidosites.

He regarded it as probable that the rocks are of later Archæan or

Cambrian age.

7. "The Ejected Blocks of Monte Somma," Part I. Stratified Limestones." By H. J. Johnston-Lavis, M.D., F.G.S.

Introductory.—The author referred to the Hamilton collection, now in the British Museum, and to the work of Prof. Scacchi, who enumerates 52 mineral species as having been found in the ejected blocks, and indicated the importance of these from a geological and volcanological point of view. His own collection contains over 600 specimens, showing the graduation from unaltered limestones, through various stages of change into numerous varieties of "true metamorphic

rocks," which, in their turn, shade into igneous rocks more and more approaching the several modifications of the normal cooled magma of the volcano. Moreover, such rocks come from depths where they have not been affected by alterations of a secondary nature.

He then gave a classification of the varieties of ejected blocks. The Tertiary rocks are but slightly metamorphosed, whilst the limestones of Cretaceous or earlier age afford an almost unlimited series of mineral aggregates. Physical changes have converted them into carbonaceous and saccharoidal marbles; next oxides and aluminates have separated, and silicates have been introduced. Such rocks come under the definition of accidental ejectamenta. They are only ejected when the apex of the crater-cavity, formed by an explosive eruption, extends below the platform of the volcano into the underlying rocks. He then traced the history of the eruptions of Somma-Vesuvius through divers phases, showing that it was only at a comparatively late period that limestone-fragments were blown out, though this had taken place long before the Plinian eruption. stratified limestones have been chosen for the first part of this paper, because their original lithological structure acts as a guide as we proceed from a normal limestone to its extreme modifications.

Part I.—The character of the limestones which underlie the platform of Vesuvius may be studied in the peninsula of Sorrento, where the mass attains a thickness of 4700 feet. They are magnesian in varying proportions. A table was given showing twentyseven analyses, made principally by Ricciardi, the amount of MgO ranging from 1 to 22 per cent. Silica rarely exceeds 2 or 3 per cent., whereas in the greater number of limestones it is absent. The bituminous matter, though a powerful colouring agent, usually exists in quantities too small for estimation, but sometimes reaches 3 per cent. Such are the materials out of which the extraordinary series of silicate-compounds have been developed; and as these materials of themselves could not form peridotes, micas, pyroxenes, &c., it is clear that the silica, alumina, iron, fluorine, &c. must have been introduced from without, viz., from the neighbouring igneous magma. The author then discussed the question of the probable methods, being inclined to favour the notion of vapour in combination with acid gases.

The bulk of the paper was occupied with a detailed description of the microscopic structure of these stratified limestones and their derivatives. The author remarked that the same metamorphic changes may be traced on a much grander scale amongst the ejected blocks, and hinted at the similarity of these changes to those of contact-phenomena as seen elsewhere, and even of regional metamorphism, the two main factors to be considered being the composition of the rock to be acted upon and that of the magma acting.

The changes which ensue in an impure limestone are, in the first place, the carbonization of the bituminous contents, which are converted into graphite; and a kind of recrystallization, approaching the saccharoidal structure, seems to have taken place, although the stratification &c. is preserved. A few grains of peridote now begin to make their appearance, chiefly as inclusions within the calcite crystals, and thus by degrees the results already recorded are effected. In the early stages only is the metamorphism selective. The order in which the new minerals seem to develop is the following:—

(1) Peridote, Periclase, Humite.

(2) Spinel, Mica, Fluorite, Galena, Pyrites, Wollastonite.

(3) Garnet, Idocrase, Nepheline, Sodalite, Felspar.

Many of these minerals are crowded with microliths, which there is reason to believe consist of pyroxene.

# XXXV. Intelligence and Miscellaneous Articles.

# SUSCEPTIBILITY AND VERDET'S CONSTANT OF LIQUIDS. BY H. E. J. G. DU BOIS.

THIS investigation, carried out in the physical institute of Strasburg University, had for its principal object to decide whether the two "constants" above mentioned are really constant within a considerable range of magnetizing forces; Silow, Schuhmeister, and Quincke, on the one hand, Stscheglajeff, on the other, having found variations of the susceptibility and of Verdet's constant respectively.

The magnetic measurements were made by Quincke's second manometric method\*; an apparatus being specially constructed in order to exactly set the manometer's narrow tube to any given angle with the horizon. When this angle is made very small, say 30', quantitative measurement becomes somewhat difficult; but the method then affords an excellent qualitative test. When the difference in susceptibility of the liquid and the adjoining gas is but one ten-thousandth of the susceptibility of water, it may still be detected by this method, first used by Quet and Verdet, and quite recently developed by Toepler and Hennig. The space above the liquid was not generally evacuated, but filled with coal-gas or carbonic acid, whose susceptibility may be neglected. By substituting oxygen for the gas, always keeping the same liquid, the susceptibility of the former may be measured in terms of that of the liquid.

The field between the poles of the large electromagnet used was measured by means of Leduc's magnetometer†, based on Lipp-

mann's mercurial galvanometer.

A Lippich's polarizer was used to determine the rotation of the plane of polarization.

The following is a summary of the results obtained:—

The susceptibility and Verdet's constant for all simple liquids, salts in solution, and gases, appear to be constant for magnetizing

\* Quincke, Wied. Ann. vol. xxiv. p. 374 (1885). † Leduc, Journ. de Phys. [2] vol. vi. p. 184 (1887) forces up to 12,500 C.G.S. (and probably up to much higher values). This was proved by direct measurement on  $\rm H_2O$ , and solutions of  $\rm FeCl_3$  and  $\rm MnCl_2$  within the range of experimental errors.

A solution of any paramagnetic salt in a diamagnetic liquid may be brought to a certain concentration at which it is magnetically "inactive" in a given field. By the qualitative test alluded to it was then found inactive in any other field; from this fact an indirect verification of the absolute constancy of the susceptibility of both the liquid and the salt in solution is easily deduced. Various salts and oxygen were thus tried, all with the same result.

The properties of solutions were further investigated at some length, specially at the concentrations for which they proved either optically or magnetically inactive; the general result being a confirmation of the assumption usually made, viz. that the action of

solvent and dissolved salt is algebraically superposed.

So-called amalgam of iron seems to behave differently from simple liquids; its magnetization appears to reach a maximum like that of massive iron. This result was calculated from some of Quincke's data by a formula deduced on the most general assumption of varying susceptibility. The reason of this probably is that the amalgam is neither a chemical compound nor a real solution, but rather an emulsion of exceedingly small particles of iron in the mercury. However, this question can hardly be decided without further experiment.

The susceptibility of oxygen (at 1 atmosphere of pressure) relatively to that of water was found to be 0.14 at 15°. It was found to decrease with temperature much more rapidly than the density,

a result published somewhat earlier by Quincke\*.

The temperature-coefficient of the susceptibility of water was

found to be a decrease of 0.25 per cent. per degree.

Besides the qualitative verification of the sign of the susceptibility and of Verdet's constant for the substances most characteristic in this respect, absolute determinations were made of the susceptibilities of a few standard substances. The values at temperature 15° are contained in the following table, the susceptibility of a vacuum being of course taken as zero (its permeability = 1).

Substance.	Density.	Susceptibility.		
Water	0.9992	$-0.837.10^{-6}$		
Alcohol	0.7963	-0.694 "		
Ether	0.7250	-0.642 ,,		
Bisulphide of carbon	1.2692	-0.816 "		
Oxygen; 1 atmosphere	0.00135	+0.117 ,,		
Air; 1 atmosphere	0.00123	+0.024 ,,		

<sup>\*</sup> Wied. Ann. vol. xxxiv. p. 442 (1888).

For the details of experiment, for the discussion of its results and of those previously obtained, the original must be referred to.

—Wiedemann's Annalen, vol. xxxv. p. 137 (1888).

# SELECTIVE ABSORPTION OF METALS FOR ULTRA-VIOLET LIGHT. BY JOHN TROWBRIDGE AND W. C. SABINE \*.

The question of the absorption of the ultra-violet rays by metallic surfaces possesses considerable interest, both from a practical and a theoretical point of view. By the kindness of Prof. Pickering, Director of the Harvard University Observatory, we were provided with a number of metallic surfaces prepared by Professor Wright of Yale College. These metallic surfaces were deposited upon glass by means of electricity. The surfaces were of gold, platinum, tellurium, palladium, copper, silver, and steel. A preliminary trial had shown us that a heliostat mirror of the same composition as that upon which the grating was ruled did not absorb light of greater wave-length than 2900. We resolved, therefore, to compare other metals with speculum metal. Since our heliostat arrangement required two mirrors to direct the light upon the slit of the spectroscope, we employed a speculum mirror for the movable mirror of the heliostat, and replaced the fixed mirror by mirrors of metals whose selective absorption we wished to compare with that of speculum metal. To our surprise, the metallic mirrors of gold, copper, nickel, steel, silver, tellurium, and palladium all reached the same limit as speculum metal. Here was a complete experimental proof that colour in no way influences the selective absorption of metals for the ultra-violet rays; for the copper mirror, which gave a strong yellow light by reflexion, was as capable of reflecting light of as short wave-length as the brilliant white surface of polished silver. Although the metallic surfaces we employed were bright, slight differences in polish undoubtedly existed, and therefore we are not justified in placing much reliance upon the evidence presented by the intensity of the photographs of the solar spectrum obtained by light reflected into the spectroscope by these various metallic surfaces. The photographs, however, can be classified according to intensity, in order of numbers as follows, number 1 indicating the greatest intensity:—1, steel; 2, gold; 3, platinum; 4, palladium; 5, silver; 6, tellurium; 7, copper.

It was evident from these experiments that selective absorption of metals is far less than the absorption exercised by the earth's atmosphere. We therefore resolved to employ the light of the electric spark between metallic terminals, in order to ascertain whether any limit of absorption could be reached. For this purpose, the light of the spark between copper terminals was reflected, by means of a mirror of the metal whose selective absorption we wished to examine, upon the slit of the spectroscope. To protect the

<sup>\*</sup> From an advance proof from the 'Proceedings of the American Academy.' Communicated by the Authors.

surface of the mirror from the effects of the spark, a thin plate of quartz was placed in front of it. It was found that the copper mirror showed no limit of selective absorption by reflexion for wave-lengths of light produced by burning copper at the limits of the copper-spectrum, that is, at wave-length 2100. The photographic plate taken by this method showed all the lines that the plates showed which were taken by the direct light of the spark unreflected and unabsorbed by any medium. The palladium mirror was substituted for the copper mirror, and also showed no limit of selective absorption above wave-length 2100. We are led to conclude, therefore, that the metallic surface of the speculum metal upon which the lines are ruled which form the diffraction-grating does not fix by selective absorption the limit of metallic spectra at 1800 to 2100. This limit more likely resides in the materials forming the sensitive emulsion with which the sensitive plates are We have found that a marked difference exists in different emulsions in regard to sensitiveness to ultra-violet light. various staining processes, which enhance to such a marked degree the sensitiveness of photographic plates to wave-lengths of greater length, do not seem to affect the limit of metallic spectra in the Thus, plates stained with erythrosine, which are ultra-violet. extremely sensitive to yellow and green light, continue to give the same limit in the ultra-violet after staining as they did before they were submitted to the staining process.

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#### ON A KIND OF ELECTRICAL CURRENT PRODUCED BY ULTRA-VIOLET RAYS. BY M. A. STOLETOW.

The researches of Hertz, E. Wiedemann and Ebert, and Hallwachs having demonstrated the influence of the ultra-violet rays on electrical discharges of high potential, I conceived the idea of trying if a similar effect could be obtained with electricity of low potential.

Two metal disks, 22 centim. in diameter, are placed vertically opposite each other in front of a lantern with a voltaic arc fed by a dynamo (12 amperes, 70 volts). The disk turned towards the lamp is of wire gauze, the other is solid; the two form a kind of condenser, of which one armature may be illuminated on its internal face through the meshes of the other.

I take any battery, and connect its negative pole to the solid disk and the gauze disk is connected with the positive pole. A Thomson's a tatic galvanometer is introduced into the circuit, which is broken by an air-space.

When the lamp is lighted the galvanometer is deflected and remains so; a kind of current traverses the circuit. Any opaque screen, or any kind of glass, placed between the arc and the gauze cause the deflections to disappear; a quartz plate only enfeebles it to a slight extent. The deflection is constant as long as the lamp acts; any irregularity is at once apparent in the changes of current.

If the poles of the battery are reversed there is only a small deflection; it seems that the illumination of the positive armature is not effective.

It is clearly the action of the ultra-violet radiation which produces here the flow of negative electricity, as in the experiments cited, the layer of air acquires a kind of unipolar conductivity.

I have repeated these experiments with batteries of 1 to 100 elements. For two Daniells, the distance of the disks being 2 to 3 millim., the deflections are 30 to 50 divisions, 1 division corresponding to  $9 \times 10^{-11}$  amperes. With 100 zinc-water-copper elements traces of a current are obtained even with disks separated by 10 centim.

Cleaning the solid disk increases the effect. The intensity of the arc has great influence. In order to investigate the laws of the phenomenon the arc must be kept constant and the comparisons be made as quickly as possible.

By observing these precautions I arrive at the following con-

clusions;—

(1) If the surface illuminated is diminished (by covering  $\frac{1}{4}$ ,  $\frac{3}{4}$  of the gauze with a screen) the current diminishes in proportion.

(2) When the distance l of the disk is varied the current varies also; but it is not inversely proportional to l, and it seems rather

to follow the law  $i = \frac{E}{a+bl}$ .

(3) When the electromotive force E which charges the disk is increased the current constantly increases; so long as E is small (to two Daniells) it is proportional to it, and then increases more slowly. The apparent resistance of the layer of air seems thus to increase with the electromotive force.

If the two disks are of different metals, their electrical difference must be allowed for in estimating the electromotive force. The proportionality of *i* to the *external* electromotive force is then masked by the difference in question. If the *total* electromotive

force makes the solid disk positive there is no effect.

This suggested to me the idea that a current might be obtained in any circuit even without a battery, provided the gauze be of a metal more positive than that of the solid disk. Thus, with a disk of perforated zinc as gauze, and a solid disk of silvered copper, I obtained a current. This is a kind of element where the illuminated air takes the place of liquid, and which acts as long as the illumination lasts, the current being maintained at the cost of the radiant energy. When the two disks are brought closer until they finally touch, the current increases to a certain limit, it then passes through zero, and changes its sign (thermoelectric effect).

By comparing the current in the condenser zinc-silver with that which one Daniell produces, I have arrived at a value of 0.97 to 1.06 volt for the difference Zn/Ag. This is accordingly a galvanometric method, for comparing the electric differences of metals,

which seems to give results agreeing with those of ordinary methods.

It would be interesting to extend this research to different gases and at various pressures. The method started enables us to investigate the electrical effects of radiation under conditions which are much simpler, and more accessible to measurement, than in the experiments of the authors cited above\*.

The effect of the voltaic arc is enormously increased by introducing certain metals; among those which I have tried, aluminium is the most effective; then come zinc and lead. These, I think, are the metals of which the ultra-violet spectrum is richest; it is also to be observed that they are the most positive metals in Volta's series.

I have made some experiments by another method. Having charged my gauze condenser by a battery, I leave it insulated under the action of the rays for some time, and I then measure the discharge-current. In order to increase the charge and retard the loss due to the rays, a large and known capacity (standard mica condenser) is joined to the illuminated condenser. In this way the resistance of the layer of air may be calculated; the results are in agreement with those obtained by the first method. If the disks are of different metals, the effect of the rays tends to equalize their potentials; and by connecting the two armatures by the galvanometer, after a sufficient time a charge-current is obtained corresponding to the electrical difference of the metals.—Comptes Rendus, April 16, 1888.

INVESTIGATIONS ON THE INFLUENCE OF MOISTURE ON THE LENGTH OF CERTAIN WOODS, AND IVORY. BY RUDOLFF HILDEBRAND.

The results of this research are summed up by the author as follows:—

(1) Within certain limits, the length of woods in the direction of their fibres depends on the proportions of water in the cell-wall, and with an absorption of water amounting to 20–30 per cent. the increase of length may amount to 0·1 to 2 per cent., according to the kind of wood.

(2) The woods are shortest when all water is withdrawn from them.

(3) Dry woods are highly hygroscopic.

(4) Woods attain their greatest length by absorbing water from air charged with it, or by complete soaking with water.

This Note was written before I knew of a recent research of M. Arrhenius (Wiedemann's Annalen, No. 4, 1888), who obtains analogous results by working either with phosphorescent air, which forms part of an electrical discharge-tube, or with rarefied air illuminated from the outside. The method of M. Arrhenius is not delicate enough for pressures above 20 millim., and it does not bring out the difference in the function between the two electrodes of the current in air.

Compare also Phil. Mag. [5] vol. xxv. p. 314 (Ed. Phil. Mag.).

(5) The length of the woods increases, from the condition of dryness, with the moisture. After the wood has attained the greatest length the absorption of water from moist air continues,

but more slowly than before.

(6) Certain kinds of wood, after being completely dried, are unable to attain the length which they have when air-dried. The behaviour of plum-tree wood is very remarkable; after reaching a certain maximum, which is inversely proportional to the increase of moisture, its length decreases.

(7) The length and weight of the woods increase with the rela-

tive moisture of the air, and decrease with it.

(8) The usual modes of treatment of wood—polishing, soaking with oil—do not cut off the influence of saturated air. The best is varnishing.

(9) In the longitudinal direction of the teeth, ivory is liable to great changes in length as the moisture varies.—Wiedemann's

Annalen, No. 6, 1888.

#### LECTURE-EXPERIMENT. BY M. P. SIMON.

There are a certain number of experiments which serve to demonstrate the fact that, when a body is heated, the rays which it emits are a function of the temperature, that they follow each other, superposing themselves in the order of the colours of the spectrum from red to violet.

A known method consists in stretching a platinum wire in the flame of a Bunsen-burner and in viewing it with a prism. The spectrum is then seen complete in the centre and diminishing

towards the edges, where it only contains red rays.

I have arranged the experiment in a different manner, which produces the phenomenon very brilliantly. A spectroscope is taken, and turned towards an ordinary gas-jet so as to obtain a spectrum; then across the slit, and very near it, a platinum wire is stretched which is made incandescent by a current, a rheostat being interposed in the circuit. In these conditions, and without heating the wire, the spectrum is traversed by a dark line. The current is now gradually passed through the wire. At a given moment the dark line will disappear in the red only. Evidently the wire emits a red radiation of the same intensity as that of the spectrum.

The experiment is continued by gradually increasing the intensity of the current. We see the wire stand out brightly in the red of the spectum, while it becomes invisible in the green, and is obscure in the violet. Gradually heating, the invisible part gradually extends towards the violet, until the entire line stands out brightly over all the spectrum. This experiment is very easily made by regulating suitably the distance of the source of light from the spectroscope, that is to say, regulating the intensity of the spec-

trum.—Journal de Physique, February 1888.

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# PHILOSOPHICAL MAGAZINE

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### OCTOBER 1888.

XXXVI. Experiments on the Birefringent Action of Strained Glass. By John Kerr, LL.D., Free Church Training College, Glasgow\*.

1. THE action of strained glass in the polariscope was discovered by Sir David Brewster, and studied by him at some length, about seventy years ago. In the most of his measurements and specifications of the effects of strain, Brewster depended upon the observation of tints in the polariscope, his optical means and methods being the same for strained media as for doubly-refracting crystals. Plates of glass were strained, either by ordinary forces or by local changes of temperature, and were placed in the polariscope, in combination with plates of sulphate of lime, or other crystals, whose birefringent actions were known in kind and quantity. In this way it was found possible to determine, with a good degree of approximation, the difference of retardations of two oppositely polarized rays, which passed through the strained medium without being sensibly separated. Brewster's principal results will come under our notice as we proceed t.

Fresnel contributed little to this part of Physical Optics except his one experiment, in which, by the action of a train of longitudinally compressed prisms, he succeeded in decomposing a pencil of common light into two separate pencils

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Phil. Mag. S. 5. Vol. 26. No. 161. Oct. 1888.

<sup>\*</sup> Communicated by the Author.

<sup>†</sup> The most of Sir David's work on the subject is described in two of his papers, in the Phil. Trans. for the year 1816.

oppositely polarized. His immediate object in this fine experiment, and in some other work which he has mentioned but left undescribed, was to dispose of doubts that had been expressed by others, as to the reality of the double refraction to which the new phenomena were referred by Brewster\*.

The next name that occurs prominently in the history of the subject is that of M. Neumann, who constructed a mathematical theory of this action, based partly on Fresnel's general theory of double refraction †. For a critical view of this theory, and of the experiments adduced in connexion with it, I may refer to Verdet's Optique Physique ‡; but, speaking for myself, and from an experimental standpoint, I must observe that Neumann's conclusions are certainly contrary to fact.

M. Wertheim, resuming Brewster's enquiry with improved means and arrangements, experimented on the subject elaborately, and with great care §. He secured a sensibly homogeneous strain, and a uniform optical field, by a proper distribution of compressing and stretching weights; and he added much to the delicacy of observation and measurement, by the employment of the sensitive tint, and of monochromatic light. He experimented also, as Brewster had already done, upon other media besides glass. Among the most important of Wertheim's general conclusions are the following:—

(1) The optical effects of dilatation and compression are contrary; and they are equal when the strains are equal.

(2) Intensity of strain and quantity of optical effect are

sensibly proportional to each other.

(3) The absolute value of the difference of retardations of the two acting rays is independent of the wave-length; and the differences of phase are therefore inversely as the wavelengths.

There are several important and interesting pieces of work, related more or less closely to what precedes, which have been done by Seebeck, Biot, Kundt, and other able experimenters; but any large extension of this historical sketch

would be out of place.

I have lately spent a good deal of time in this difficult and interesting field; and I proceed to offer a few notes of my experiments. For a condensed view of the questions proposed and results obtained, I need only refer to the enunciations of the successive propositions throughout the paper.

2. Jamin's Interference-Refractor for Polarized Light.— This is the principal measuring-instrument used in the experi-

\* Oeuvres d'Augustin Fresnel, tome i. p. 713.

† Poggendorff's Annalen, liv. p. 449 (an. 1841). ‡ Tome ii. p. 373. § Annales de Chimie et de Physique [3] xii. p. 96, &c. (an. 1854).

ments: it is represented in the adjacent diagram, in horizontal section through the source of light L and the observer's eye E.

Fig. 1.



A and B are two blocks of Iceland spar, of precisely equal thickness, placed with their faces parallel, and principal sections horizontal. A pencil \* of lamp-light, through a vertical slit at L, falls first on a Foucault's prism, and is polarized by it in a plane at 45° to the vertical; it is then doubly refracted in the spar A, and the emergent pencils pass immediately through a half-wave plate P, which is so placed as to interchange the two planes of polarization. Ordinary ray and extraordinary in the crystal A are thus extraordinary and ordinary in the crystal B; and the birefringent action of A is neutralized by that of B. The light enters A and leaves B as a single pencil; but in the space between P and B it passes as a couple of pencils V and H, about 14 millimetres apart, and polarized in planes respectively vertical and horizontal. The pencil emitted from B is received at E through a Nicol's prism, which is placed as for extinction with the Foucault at L. When the principal sections of A and B are very nearly parallel, the slit L is seen crossed by a set of fringes, which are due to differences of retardation of corresponding rays of the pencils V and H. By fine screwmovements of the spar B, the fringes are widened or narrowed at pleasure, and raised or lowered over a fine wire of reference which crosses the slit L.

At D are shown, in section, the two plates of a Jamin's glass compensator. These are slips of parallel-surfaced glass, of equal thickness, attached to the horizontal axis of a small piece resembling a Wollaston's goniometer, and bearing a finely divided circle with vernier. The plates are inclined to each other at a small and constant angle which is chosen by the observer; and when either plate is vertical, it is traversed normally by the corresponding pencil V or H. When the compensator is turned through any angle, the retardations of the two pencils in the plates D are changed unequally, and the fringes rise or fall definitely over the wire of reference. All the preceding pieces are established on a solid optical bench.

<sup>\*</sup> Rather a system of pencils; and similarly afterwards.

My model of this instrument is national property: it was constructed for me by M. Lutz with his usual skill, and goes far to realize the inventor's very exacting conception. With the instrument as it stands, it is not very difficult to measure a difference of retardations of the two pencils, true probably to the hundredth of an average wave-length, that is to the five millionth of an inch of path in air. Under very favourable conditions (careful setting of the pieces, moderate range of effect, absence of tremors, &c.), the error of a single determination of effect should not exceed the twentieth part of an average wave-length.

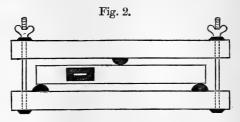
3. Designation of the two acting sets of rays.—The two separated systems of rays in the interference refractor, between the half-wave plate and the second spar, will be designated briefly, throughout this paper, as the pencils V and H, their planes of polarization being thus distinguished as vertical

and horizontal respectively.

### Proposition I.

If a plate of glass, compressed or extended in one direction parallel to its faces, be traversed normally by two pencils of light, which are polarized in planes respectively parallel and perpendicular to the direction of strain, then, both pencils are retarded by the strain in the case of compression, and both are accelerated by the strain in the case of tension.

4. The discovery of this fundamental proposition was made with a bent plate and the interference refractor. The



glass plate shown in the diagram is 10 to 12 inches long,  $\frac{1}{8}$  to  $\frac{3}{4}$  thick,  $1\frac{1}{4}$  to 2 wide. Its two sides are ground flat, sensibly parallel to each other, and perpendicular to the plate-faces. The three small semicircles in the diagram are bearings of ebony, semicylindrical and equal, through which the bars of the screw-press act upon the plate. The small rectangle on the upper half of the plate\* is a slit-screen of paper, which is pasted on the glass in a position chosen carefully with the help of the polariscope, so that the slit lies along the middle

<sup>\*</sup> The plate stands in the experiments with its length vertical.

of the neutral band in the strained plate, with nearly half an inch of screen between it and each of the glass margins. The screw-press being clamped firmly to a heavy vertical stand, the slit-screen is brought into the course of the two pencils of the refractor, as shown in section at F in the diagram of art. 2: the refractor also is supposed to be so arranged, that a rise of the fringes indicates a relative retardation of the pencil V. Things being thus prepared, the experimental proof of the proposition extends through the four following cases, which are got by simple displacements of the plate-stand.

(1) V through compressed margin, H through slit; strain raises the fringes; V is retarded relatively, and there-

fore absolutely.

(2) V through extended margin, H through slit; strain lowers the fringes; V is accelerated relatively, and therefore absolutely.

(3) H through compressed margin, V through slit; strain lowers the fringes; V is relatively accelerated, and H

therefore is absolutely retarded.

(4) H through extended margin, V through slit; strain raises the fringes; V is relatively retarded, and H therefore

is absolutely accelerated.

I have reasoned here as if the strains in the margins of the plate were pure vertical compression and pure vertical tension respectively, and also as if there were no strain behind the slit, in the neutral part of the plate. It is certain that things are not exactly thus; and objection may therefore be made to the proof as wanting in rigour. If any doubts remain on this account as to the truth of the proposition, they will

disappear very soon.

The results of these experiments are quite regular. When a good plate is put in position unstrained, and the central fringe is brought on the wire of reference, a quarter turn of either screw of the press gives a clear displacement of the fringes, always in the right direction of rise or fall according to the proposition; and as the strain is gradually increased, the displacement of the fringes also increases regularly, through one, two, three, or more fringe-widths, till the plate breaks. The effects are equally clear with different kinds of glass, and with different thicknesses.

In the course of a few repetitions of the experiments, there was another important result that presented itself: the four preceding cases fell clearly into two sets—(1) and (2) as cases of strong action, (3) and (4) of weak action; but this de-

serves a detached and formal statement.

#### Proposition II.

Of the two pencils in the foregoing proposition, the one which has its plane of polarization parallel to the line of strain is the more sensitive, being most retarded or most accelerated of the

two by any given compression or tension.

5. The proof is simplified by a little change of method. The slit-screen is removed from the plate, and a narrower screen is substituted, covering the neutral band and leaving more than half an inch of glass margin on each side. The experiments may be taken in four cases as formerly, and in the same order.

(1) and (2). Both pencils through one margin, V being outside, that is, in the place of greater strain. The effects are not clearly distinguishable in any respect from those in (1) and (2) of the last article, the pencil V being relatively retarded by the strain in the compressed margin, and rela-

tively accelerated in the extended margin.

(3) and (4). Both pencils through one margin, H being outside, or in the place of greater strain. The pencil H is relatively and faintly retarded by the strain in the compressed margin, relatively and faintly accelerated in the extended margin. The effects are of the same kind as those in (3) and (4) of the last article, but fainter in a striking degree (for any given strain) than those in (1) and (2). I find, indeed, that the effects in the present cases (3) and (4) are sometimes barely or not at all perceptible, especially when the plate and margins are very wide, and this even with plates which are very thick and strained nearly up to fracture. As the pencils pass now through one margin, they are both accelerated or both retarded; and it follows evidently that the pencil V, which is in the place of weaker strain, is the more sensitive.

Like the former experiments, these improve on repetition, the clear contrast between the two pairs of cases coming out with perfect regularity.

#### Proposition III.

To explain the action of directionally strained glass in the common polariscope; or to infer Brewster's property of strained

media from facts more fundamental.

6. Brewster's property may be described thus. When the strained plate of proposition I. is placed between a pair of crossed Nicols, it acts as a birefringent medium; and if the plate of glass be superposed upon, or merely compared with, a plate of uniaxal crystal with optic axis parallel to line of strain, the same component ray is relatively retarded in both

plates (1) when the glass is compressed and the crystal negative, and (2) when the glass is extended and the crystal

positive.

Suppose optic axis and line of strain both vertical. Let O and E be the retardations of the ordinary and extraordinary pencils in the crystal, V' and H' the strain-generated retardations of the same pencils (V and H)\* in the glass. We know that the sign of the difference E-O is the nominal sign of the crystal. The relative retardation H'-V' is therefore negative in the case of vertical compression, and positive in the case of vertical tension. But it follows from the two preceding propositions, that strained glass must act in the polariscope according to these very laws; for (1) in the case of vertical compression, V'>H',

$$\therefore H'-V'<0$$
;

and (2) in the case of vertical tension, V' < H' < 0,

$$H' - V' > 0$$
.

According to Brewster's usual manner of putting his facts, the extraordinary ray is relatively accelerated in negative crystals, and relatively retarded in positive crystals; and similarly, in glass vertically strained, the component pencil H is relatively accelerated in the case of compression, relatively retarded in the case of tension. What was thus presented to Brewster, in the case of glass vertically compressed, as a relative acceleration of the component pencil H, is now exhibited more definitely, as an absolute and excessive retardation of the other component pencil V; and similarly, in the case of vertical tension, the relative retardation of H is now exhibited as an absolute and excessive acceleration of V.

These results are independent of all hypotheses; they neither presuppose nor exclude any particular laws of refraction, ordinary or extraordinary, in the strained medium. The experimental interpretation of Brewster's property will

be simplified and completed further on.

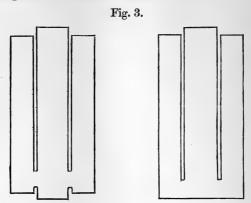
7. The winged plate. This new piece is shown in two

forms in the diagram on the following page.

It is a parallel-surfaced plate of glass,  $\frac{1}{4}$  to  $\frac{1}{2}$  inch thick, divided into a central pillar and two wings, by slits ground through the plate for the greater part of its length, like fine saw-slits through a plank. The central pillar is, as nearly as possible, a rectangular parallelepiped, its two ends being ground

<sup>\*</sup> Not the V and H of art. 3, but similarly named for the same purpose, that is, to indicate briefly and clearly the directions of their planes of polarization.

with particular care. Width of pillar and of each wing about  $\frac{1}{2}$  inch, length of slit about  $2\frac{1}{2}$  inches.



The screw-press is a rectangular frame of metal, with two strong and fine-threaded screws passing through the top, and bearing on a massive sliding piece of metal which is guided by the two sides of the frame. The winged plate stands vertically between the plane base of the frame and the sliding piece, being separated from the base by a dozen folds of tin foil, and from the sliding piece by plates of wood and indiarubber. When the whole piece is placed in a polariscope, and the screws are worked forward with proper care, there is an intense effect of pure vertical compression obtained in the central pillar, without a trace of effect in either wing. Pillar and wings act as parts of one unbroken plate, which differ only in regard to strain.

The first use made of this piece, and of a similar plate arranged roughly for vertical tension, was to revise the proofs of propositions I. and II. Both propositions were fully verified, the effects being sensibly neither better nor worse than those obtained already with the bent plate. Details are

omitted as unnecessary.

# Proposition IV.

Things being still arranged as in propositions I. and II., it is required to measure the strain-generated retardations of the two pencils, and to show that, for the same strain, the greater of these effects is exactly or very nearly twice the less.

8. My earliest results in this direction were obtained by some rough measurements with the bent plate and the refractor. The plate was mounted as in the diagram of

art. 4, and had set so well into its bearings by usage, that any moderate strain gave equal optical effects in its total rise and total fall. Beginning with V through either margin and H through the slit, the compensator at zero, and the central fringe on the wire of reference, the plate was then moderately strained, and the displaced fringe was brought back to its first position by the compensator, which was then read. The places of V and H in margin and slit were then interchanged by a simple displacement of the plate-stand, the compensator was again brought to zero, and the central fringe to the wire of reference; the plate was then carefully unstrained, and the displaced fringe brought back as formerly to its first position by the compensator, which was again read. The two readings were taken as measures of the two straingenerated retardations.

Of a number of measurements taken in this way, I give here the last eight, the numbers in successive columns being the pairs of readings for the successive strains, left as they were found, in vernier-units (about 84 to the wave-length). The strain was tension in the first four columns, compression

in the others.

103	69	39	74	75	92	<b>55</b>	85
49	34	21	37	38	45	27	43

Approximately, therefore, the greater retardation is twice the less.

9. Measurements of a more accurate kind, but through a rather small range, were taken next with the winged plate and refractor, checked by a Jamin's quartz compensator. The plate was tested beforehand by the quartz compensator, and was found to be so well fitted to its bearings, that a given strain of moderate intensity could be recovered perfectly, a good number of times in succession: the plate was then placed on a suitable stand, in the course of the pencils of the refractor.

(1) V passing through the middle of the central pillar, and H through a wing, the given strain (vertical compression) was applied, and its effect was neutralized by the glass compensator, which was then read. The plate was then unstrained, and the reverse effect was compensated and the compensator again read. If the two readings differed in arithmetical value, their average was taken as the measure of V', the strain-generated retardation of the pencil V.

(2) The plate-stand was moved across the pencils, till H took the former place of V in the winged plate; the operations (1) were repeated, and the average of the two new

readings were taken as the measure of H', the strain-

generated retardation of the pencil H.

(3) The winged plate was then transferred to another table, and put in line with the quartz compensator at zero, between two crossed Nicols each at 45° to the vertical: the given strain was again applied, and its effect compensated; and the corresponding reading of the quartz compensator was taken as the measure of the difference V'—H'.

In the course of the experiments, there were precautions taken and checks applied, which it would be tedious to describe; and in this way a good many of the measurements were thrown out of account; but as the result of a day's work there were found to be, among the later measurements, about half a dozen identical sets of readings,

$$V'=55$$
,  $H'=27\frac{1}{2}$ ,  $V'-H'=96$ ,

for which all the tests had been fairly satisfied. Reduced to wave-lengths (or divided by 84, 84, 299 respectively), the values are

·654, ·327, ·321;

and these measures of V', H', V'-H', are sensibly as the numbers 2, 1, 1. A second day's experiments, with smaller strain, gave similarly

·439, ·219, ·220;

and a third day's work, with strain again increased, gave

·635, ·317, ·314.

It appears therefore, by this method, that the two absolute

retardations in question are sensibly as 2 to 1.

10. In a third set of measurements, the winged plate and refractor were used alone, and the range of measured effect extended to three wave-lengths. V passing through the middle of the central pillar, and H through a wing, the plate was strained, and the effect was compensated and measured. The strained plate was immediately moved across the pencils till H took the place of V; and in this position the plate was unstrained, and the effect was compensated and measured. The next pair of measurements were generally taken in the contrary order (H' to V').

The ratio of V' to H' was measured many times by this method, and with great care. The successive determinations were not very concordant: with several exceptions they lay between 2.05 and 1.95; the majority lay between the closer limits 2.03 and 1.97; and there was no clear preponderance of values above 2, or of values below 2. A number of the

earlier measurements being left out as less accurate, the average of the remaining eighty determinations, carried to 4

figures, was 2.004.

Upon the whole, from these measurements, and from others taken recently by another method, I conclude that the straingenerated retardation of the pencil H, in glass vertically compressed, is sensibly equal to half the corresponding retardation of the pencil V, its value in any case being probably as accurate, when so inferred from a well measured retardation of V, as when found itself by actual measurement.

#### PROPOSITION V.

Strain-generated retardations, absolute as well as relative, are

sensibly proportional to the strain.

11. The effect of directional strain which is observed in the polariscope, that is, the difference of strain-generated absolute retardations of the two component rays, varies directly as the strain. This was roughly proved by the experiments of Brewster, and has been already quoted as a general conclusion drawn by Wertheim from a large number of accurate measurements. On this part of the subject, and for illustration rather than proof, I may present a set of measurements of my own,

which I took at an early stage in my experiments.

A fine rectangular bar of plate glass, with a small connecting piece elamped upon it at each end, was suspended vertically in front of a Jamin's quartz compensator (between a pair of crossed Nicols each at 45° to the vertical), and was strained by a suspended weight; and the effect of the strain so impressed was compensated and measured. The dimensions of the bar in millimetres were—length about 150, thickness (along the ray) 6.57, breadth 12.95; and the only weights applied were one of 56 pounds (total), and another of 28 pounds (total). One hundred fairly concordant measurements were taken with each of the weights, and the average effects of the strains in the two cases (56 and 28) were found to be, in wave-lengths,

#### ·0965 and ·0483.

In Wertheim's experiments, the closely approximate proportionality of optical effect to intensity of strain was found to hold good, through the whole of the large range of effect examined, with exceptions easily understood in the case of very feeble strains.

Knowing then that the relative retardation of V is proportional to the strain, and that the absolute retardations of V and H and the relative are as the numbers 2, 1, 1, we infer

that the absolute retardations also are sensibly proportional to the strain.

#### Proposition VI.

To analyse the two strain-generated absolute retardations which are compared in proposition IV., these retardations being now viewed as composite effects of the strain, due partly to change of refringent power of the glass, and partly to change of thickness of the plate.

12. An elementary solution of this delicate problem is attempted under the present proposition and the two follow-

ing, by means of the winged plate and refractor.

When the winged plate is unstrained, let e be its thickness, and m its index of refraction; when the central pillar, standing vertically, is compressed by a given weight, let  $e + \delta e$  be its thickness,  $m + \delta m$  and  $m + \delta' m$  its indices of refraction for the pencils V and H respectively; also let m' be the index of the medium in which the plate is immersed. If the two pencils of the refractor pass through the plate, V through strained pillar, and H through unstrained wing, the straingenerated difference of their retardations

$$= (m + \delta m) (e + \delta e) - (me + m'\delta e)$$
$$= e\delta m + (m - m') \delta e = V'.$$

In the same way, the difference of retardations of H through strained pillar and V through unstrained wing

$$=e\delta'm+(m-m')\delta e=H'$$
.

Let the winged plate be immersed first in common air (index=1), and then in any convenient liquid (index=m'); and let a and a' be the values of the retardation V', measured by the refractor in the two cases respectively; then

$$e\delta m + (m-1)\delta e = a, \dots$$
 (1)

$$e\delta m + (m-m')\delta e = a'$$
. . . . (2)

Hence immediately,

$$(m'-1) \delta e = a - a', \ldots (3)$$

$$(m'-1) e \delta m = (m-1) a' - (m-m') a$$
 . . (4)

Eqs. (3) and (4) indicate a complete experimental solution of the first part of our problem, that namely which regards the pencil V; for these equations enable us to express the two terms of the first member of equation (1) separately, in terms of only the measured quantities m, m', a, a'.

In the same way, if b and b' be the measured values of

the retardation H' in the same two cases of air and liquid respectively, then,

$$e\delta'm + (m-1)\delta e = b,$$
 . . . . (5)  
 $e\delta'm + (m-m')\delta e = b',$  . . . . (6)

Eqs. (5) and (6) give an expression for  $e\delta'm$  and a second expression for  $(m-1)\delta e$ , both involving measured quantities only; but if the quantities a and a' have been measured accurately, the difficult and very tedious measurements of b and b' can be avoided in a way that seems to be quite safe though circuitous; for by eqs. (1) and (5), and by prop. iv.

$$e\delta'm - e\delta m = b - a = -\frac{a}{2} \dots \dots (7)$$

The solution of our problem is contained in the equations (3), (4), (7), or in the three following:—

$$(m-1)\delta e = \frac{m-1}{m'-1}(a-a'),$$

$$e\delta m = a - (m-1)\delta e,$$

$$e\delta' m = e\delta m - \frac{a}{2}.$$

We come now to the measurements.

#### Proposition VII.

If a winged plate, whose index of refraction\* is 1.53, be immersed successively in atmospheric air and in water, the differences of retardation of V through strained pillar and H through unstrained wing, produced by the same vertical strain in the two cases, are sensibly as 100 to 69.

In other terms, and in the notation of last article, if m=1.53, and m'=1.33, then a-a'=.31a.

13. Winged plate and refractor are used as before, but there are some new arrangements. Two strong wooden posts are erected on opposite sides of the optical bench; they are bound together at their lower ends, and bracketed to the table, so as to form one rigid piece with it; and they are connected at their upper ends by a massive bar of iron, which is directed horizontally at right angles to the optic bench. Projecting vertically downwards from the middle of the iron traverse, and forming one piece with it, there is a strong

rectangular frame of metal, which serves as a stand and press

<sup>\*</sup> Measured on a small prism taken from the same piece as the winged plate, and certainly true to less than 3 per cent.

for the winged plate. This frame descends, without contact, into a water-tight cell of uniform thickness (about 4 centimetres), which stands in a fixed position, with its limiting panes vertical. The winged plate, in a constant vertical position, is immersed thus in the same vertical plate of air and of water successively; and when all the pieces are properly placed, the pencils of the refractor pass normally through the composite plate, V traversing the strained pillar of the winged plate, and H an unstrained wing. is impressed by a constant weight of 56 lbs., which is applied by a sort of balance-beam, to a bolt that passes through the iron traverse and acts on the sliding piece of the press. The beam is raised and lowered by two assistants, who stand on opposite sides of the table. Generally, the plate was in air one half of the day, and in water the other; and a good many measurements were taken in both cases each day.

As the range of measured effect was very small, the probable error of observation was relatively great; there were also accidental disturbances, which could neither be wholly prevented nor taken exactly into account. A good deal of time was spent in attempts to get consistent readings. There was always a clear decrease of effect from the case of air to that of water; but the decrease was very irregular, oscillating about 30 per cent. through a considerable range. Even the average of successive tens varied from about 25 per cent. to 36. Latterly, when all known precautions were taken, the results agreed better, but never quite satisfactorily. I give here the results of the last four sets, each of the numbers being an average of about one hundred measurements:—

Effect in air = 1632	.1712	.1712	.1712
Effect in water = 1115	·1175	·1200	·1187
Fall per cent. $= 31.7$	31.3	29.9	30.7

The smallness of values in the first column was understood to

be due to heterogeneity of strain.

In a later set of measurements the method was different. The plate was permanently immersed in water, and the strain was produced by pressure of two screws on the sliding piece of the press; the effect in water was measured as in the former experiments; but the effect in air was inferred (by prop. IV.) as the double of the effect given by the quartz compensator, the latter effect being evidently the same in air as in water. One advantage of the method was the comparatively large range of effect measured; but along with this there were some disadvantages.

Several hundreds of measurements were taken in this way

with particular care. The fall per cent. of effect from air to water oscillated as formerly about the value 30, the agreement of successive results being rather better than in the former experiments, but not yet satisfactory. The average of all the determinations, carried to four figures, was 31.08; and this is pretty close to the average of the four percentages noted above, which is 30.9.

Upon the whole, and in the meantime, the decrease in question must be taken, in round numbers, as 31 per cent.

#### Proposition VIII.

Of the two strain-generated absolute retardations compared in prop. IV., one half of the greater is the only part which is produced by change of refringent power of the glass, the other half of the greater, and the whole of the less, being due to change of thickness of the plate.

14. Returning to the final equations of art. 12, and substituting for m, m', a-a', their values given or measured in art. 13, namely, 1.53, 1.33, .31a, we find

$$(m-1) \delta e = \frac{53}{33} \cdot \frac{31}{100} a = \cdot 498a,$$
  
 $e\delta m = a - \cdot 498a = \cdot 502a,$   
 $e\delta' m = \cdot 502a - \cdot 5a = \cdot 002a.$ 

These quantities are very nearly equal to 5a, 5a, 0, which are the values that satisfy the proposition. The common value of the differences, which is 002a, is a quantity too small to be detected with certainty in the experiments, being less than the 2500th part of a wave-length; and this important proposition may therefore be accepted in the meantime, as true exactly or approximately.

Cor. Returning to eq. (6) of art. 12, we see that b'=0 when m'=m, and that b'<0 when m'>m. The latter case has been realized with the preceding winged plate immersed in carbon disulphide.

Inferences equally obvious, but more important, are stated in the next two propositions.

#### Proposition IX.

The action of directionally strained glass in the common polariscope, upon light crossing the line of strain at right angles, is due exclusively to strain-generated change of velocity of the component ray which has its plane of polarization parallel to the line of strain.

Suppose the plate vertical, and the line of strain also

vertical; then, in the notation of art. 12, the strain-generated relative retardation of the component ray H

$$= \{e\delta m + (m-1)\delta e\} - \{e\delta m + (m-1)\delta e\}$$
$$= -e\delta m.$$

Thus, in glass vertically compressed, the relative acceleration of the component ray H is produced exclusively by a decrease of velocity of the component ray V; and similarly, with change of sign, in the case of vertical tension. This completes the solution of prop. III.

#### Proposition X.

In the glass plate of prop. VII., strained homogeneously in one direction parallel to its faces, the strain-generated variations of the thickness (e), and of the index (m) for light incident normally, and polarized in a plane parallel to the line of strain, are such as to satisfy approximately the equation

$$\frac{\delta e}{e} = \frac{\delta m}{m-1}.$$

For the equality of  $e\delta m$  and  $(m-1)\delta e$  has been proved by experiment.

#### Proposition XI.

To find the effect of directional compression or tension in glass, upon light passing along the line of strain.

15. I have made several attempts on this part of the subject at different times, and I begin here with the latest. The particular plate employed in the experiment is a rectangular parallelopiped of light optical flint (of Chance's), \frac{1}{4} inch thick, 6 inches long, and  $2\frac{1}{2}$  wide, its two ends  $(2\frac{1}{2}$  by  $\frac{1}{4})$  very well planed and polished, so as to give good vision through the glass, along the length of the plate. This piece is fixed to a suitable stand by one of its edges, with its faces horizontal, so that the two pencils of the refractor (from a vertical and very narrow lamp-slit) traverse the two ends at right angles, one of the pencils passing as close as possible to the outer lateral surface (6 by 1/4) through the whole of its length. these trying circumstances, the fringes are obtained almost as well through the glass as through air, the plate being a singularly good one, the glass homogeneous and isotropic, and the surfaces of incidence and emergence accurately plane and parallel.

To strain the glass moderately, and in a manner sufficiently regular for a qualitative experiment, an assistant lays his bare

arm gently along the outer lateral surface of the plate for five seconds, and then withdraws it. Moderate though the heating is, the fringes are largely affected by it, being rapidly displaced and inclined, and before the end of the five seconds deformed even to extinction. In 1 to  $1\frac{1}{2}$  seconds they reappear distinctly, but so placed as to indicate a large relative retardation of the pencil which is next the heated surface, and so inclined as to indicate an extremely rapid decrease of the optically effective strain from the heated surface inwards. As the observation is continued, the fringes fall back to their initial positions and directions, quickly at first, then more and more slowly, for 4 or  $4\frac{1}{2}$  minutes. When the experiment is repeated with a time of heating as short as 2 seconds, or even 1 second, the effects are distinct enough though less intense, the fringes being well displaced and inclined, without extinction or great deformation. This experiment was often repeated, and the effects were perfectly regular.

When the plate, as it stands, is examined between crossed Nicols, the effect of the regular heating is very faint, being easily neutralized by a hand-compensator of thin glass. Directional strain across the rays is therefore out of account in the principal experiment, which is found indeed to give sensibly the same quantity of effect whether V or H is next the heated

surface.

The birefringent action of a glass plate, strained by change of temperature along one edge, and traversed by light perpendicular to the faces, was examined carefully by Sir David Brewster, and the phenomena were fully discussed afterwards by Sir John Herschel\*. From their results it is evident, that the predominant strain in our heated plate is compression along the length at the heated edge and at the opposite edge, with a diffuse tension along the length in the intermediate parts of the plate: and this is proved easily as follows.

When the plate is placed between crossed Nicols, with its length vertical, and its faces perpendicular to the rays, the effect of the regular heating indicates pure vertical compression at the heated surface, falling off rapidly inwards, and disappearing at  $\frac{1}{8}$  to  $\frac{1}{4}$  inch from the surface. Inside of this, about  $\frac{1}{2}$  inch from the surface, which is the place of the inner pencil in the principal experiment, there is generally an effect of the contrary kind, but so faint as to be clearly out of account, in comparison with that close to the heated surface. When the plate is in the same position, and the refractor is employed instead of the polariscope, the effect of the regular

heating is found, accordingly, to be compression along the length of the plate, very intense at the heated surface, and diminishing very rapidly inwards. The effect obtained in the principal experiment with the heated plate admits therefore of only one explanation:—a ray along a line of compression is

retarded by the strain\*.

This is not such a simple result as it may at first appear to be: for the observed retardation is the sum of two terms, corresponding to  $e\delta m$  and  $(m-1)\delta e$  of the retardation a of art. 12, the first due to change of refringent power, and the second due to change of thickness of the glass along the rays; and the experiment gives us no information as to the ratio of these terms; nor do we certainly know as yet even the sign of the first term. In this connexion I must mention some

earlier experiments with a bent plate.

16. The plate was taken from the same piece of light flint as the heated plate of the last article, and was of the same length, but narrower; and it was strained in the same way as the bent plate of art. 3. It was fixed in the screw-press with its faces horizontal, so that the two pencils (vertical and very narrow) of the refractor traversed it along its length, one pencil very close to a lateral surface, and the other at or very near the middle of the plate. The action of this bent plate was not perfectly regular, the strains being complex, partly along the pencils and partly across: but upon the whole, and quite clearly, the effects were exactly contrary to those already described as given by the heated plate, a ray along a line of compression being relatively accelerated by the strain, and a ray along a line of tension relatively retarded.

To explain the contrariety of effect in the heated plate and the bent, consider the two terms of the resultant effect, as they are particularized in the end of last article. For light along the line of strain, assume that the second term is absolutely the greater of the two†. Then (1) in the bent plate, the glass is evidently shortened by the strain along a line of compression, and therefore both the corresponding second term and the total effect are accelerations; and (2) in the heated

<sup>\*</sup> A ray along a line of tension is of course accelerated by the strain. This effect is obtained very distinctly when the plate is placed as in the principal experiment; and the lateral surface, instead of being heated, is cooled by the rapid evaporation of a little ether.

<sup>†</sup> The assumption is apparently justified by what we know of the laws of deformation of glass under directional stress, taken in connexion with prop. VIII., which asserts the *equality* of the two terms when the light is *perpendicular* to the line of strain.

plate, the compression being really a small dilatation against resistance, the glass is *lengthened* along a line of *compression*, and the resultant effect for light along that line is a *retardation*.

There is one thing, however, that I have neglected here, perhaps unwarrantably, and that is the variation of index with temperature (apart from strain) in the heated plate.

#### PROPOSITION XII.

For light passing along the line of strain, as for light perpendicular to that line, the velocity of transmission is diminished by the strain in the case of compression, and increased by the

strain in the case of tension.

17. In seeking for a rigorous proof of this proposition, I have met with greater difficulties than in any other part of the subject; but now, after many trials, I find that the preceding experiment with the heated plate, when properly modified, serves the purpose perfectly. In that experiment, as described in last article, the observed retardation is a complex effect, due apparently, but in degrees not known, to these four immediate causes—(1) strain along the rays, (2) strain across the rays, (3) local change of temperature of the medium, (4) local change of length of the plate—difference of actions on the two pencils being understood for each of the four.

In the new experiment, the cause (3) is practically eliminated thus: the light passes near one edge of the plate, and the heat is applied for several seconds along the opposite edge, which is 2 and  $2\frac{1}{2}$  inches distant from the pencils. The effect of (4) is eliminated by virtual immersion of the plate in Canada balsam, this body having exactly the same index (1.58) as the plate. The effect of (2) may be safely neglected.

As in the former experiment, the plate is laid horizontally, and the light passes along its length, one pencil almost grazing the lateral surface. Close to the plate, in front of the two ends, and in the course of the two pencils, there are two small panes of thin parallel glass, which are supported in fixed positions independently of the plate, so as to form virtually the two ends of a constant and fixed cell; and the interval (about '7 millim. wide) between panes and plate are filled with Canada balsam. When the pieces are placed with proper care, I find that the fringes given in the refractor, through the composite plate (flint, balsams, and panes), are more than sufficiently good, being finer than those given formerly through the single plate of flint.

Things being thus prepared, a flat bar of iron, at a tempe-

rature a little above 100° C., is laid along the remote edge of the plate for a measured time, 3 to 6 seconds. The effect in the refractor is as distinct and regular as possible, and indicates a relative retardation of the pencil which is close to the edge. Though the temperature of the source is higher than in the former experiment, the effects are much less intense, the range of displacement of the fringes being much smaller (one third to two thirds of a fringe-width), and their changes of inclination much less marked. To explain this decrease of effect, we have to remember that the compression along the length of the heated plate is much more intense at the heated edge than at the opposite edge, and also much more concentrated, much more rapid in its rate of decrease from the lateral surface inwards: we have to remember also that, in the old experiment, there is a considerable inequality of temperatures, (with some consequent inequality of indices), for the two pencils. Upon the whole, this twefth proposition appears to me to be proved experimentally beyond objection.

#### PROPOSITION XIII.

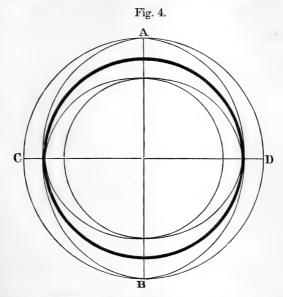
To specify the wave-surface in directionally strained glass.

18. As the line of strain is an axis of physical symmetry, we may assume that the directions of the three principal elasticities are respectively parallel and perpendicular to that line, and that the elasticities in directions perpendicular to it are Hence we infer, by the principles of Fresnel's theory, that the wave-surface in directionally strained glass is similar to that in uniaxal crystals. From Brewster's property also (art. 6) it follows that the wave-surface is of the negative class (the spheroid oblate) in the case of compression, and of the positive class (the spheroid prolate) in the case of tension. The results of the preceding experiments carry us a step further; they enable us to connect definitely the wave-surfaces in the medium strained and unstrained. Our final hypothesis may be stated in simple terms, by reference to the adjacent figure, which contains five curves of the second degree, upon rectangular axes AB and CD through their common centre. The required sheets of wave-surface are represented by these curves in principal section, that is, in plane central section along the line of strain AB; so that the sheets are generated by revolution of the curves round AB.

(1) Strain zero. The wave-surface for this case is not in question, but is required as a term of comparison: it is represented, for a given time of propagation, by the mean curve in

the diagram, the primitive circle.

(2) Compression along AB. As the strain increases from zero, the wave-surface for the given time contracts, and breaks



up into two sheets, represented by the two inner curves, ellipse and circle, the ellipse touching the new circle in points of A B, and the primitive circle in points of C D.

(3) Tension along AB. As the strain increases from zero, the wave-surface for the given time expands, and breaks up into two sheets, represented by the two outer curves, ellipse and circle, the ellipse touching the new circle in points of AB,

and the primitive circle in points of CD.

19. The matter of last article may be presented otherwise thus, in the ordinary language of Physical Optics. Glass in a state of directional strain acts on light as a uniaxal crystal, with optic axis parallel to the line of strain, the ordinary index and the extraordinary being equal to  $m(1+\alpha)$  and m respectively, where the small number  $\alpha$  is positive in the case of compression, negative in the case of tension, and (it should be added) sensibly proportional to the strain.

The elasticities of the medium, (1) in the absence of strain, (2) along the line of strain, (3) at right angles to that line, are as the numbers  $1, 1, 1-2\alpha$ , where the small number  $\alpha$  (as above) is positive in the case of compression, negative in the case of tension, and sensibly proportional to the strain. It is surely not an accident, that these optical properties of

glass, thus inferred, are so remarkably similar to the acoustic properties of the monochord.

20. I conclude, for the present, with several of the simpler inferences that may be drawn from the preceding specification

of wave-surface.

(1) Consider Fresnel's experiment with compressed prisms. The light in that experiment is refracted in a plane perpendicular to the line of strain. We see therefore, by reference to the diagram of art. 18, that one of the polarized pencils (the ordinary) is deviated by the strain, and the other not. I have not attempted to verify this inference directly by experiment.

(2) Consider a plate which is strained in one direction parallel to its faces, and a polarized ray which is incident upon it in the principal section, that is, in a plane parallel to the line of strain. By calculation based on art. 18 or 19, I find that the difference of retardations of the two transmitted rays varies directly as the cosine of the (primitive) angle of refraction. By exact measurements with a quartz compensator, through a considerable range of incidence (0° to 70°), I have succeeded in verifying this inference perfectly.

(3) Consider a polarized ray, which is incident on the same plate in a plane perpendicular to the line of strain. Both refractions are ordinary, and the difference of retardations of the two transmitted rays varies inversely as the cosine of the

angle of refraction.

(4) Inferences (2) and (3) explain the following proposition of Brewster's :- "If a plate of glass in a state of compression or dilatation is inclined to the polarized ray in a plane parallel to the axis of dilatation on compression, the tints will descend in the scale; but if it is inclined in a plane at right angles to these axes, the tints will ascend." But here it should be noticed, that Brewster's order of ascending tints is the same as the order of Newton's rings from central black outwards, that is, the order of increasing difference of retardations.

Glasgow, August 25, 1888.

XXXVII. Wave-lengths of Metallic Spectra in the Ultra-Violet, By John Trowbridge and W. C. Sabine\*.

#### Introduction.

THE Catalogue of Metallic Spectra, revised by a Committee of the British Association and published in the of the British Association, and published in its volumes

\* From an advance proof from the 'Proceedings of the American Academy.' Communicated by the Authors.

for 1885 and 1887, is an extremely valuable contribution to the subject of spectrum analysis; it contains the material for future generalization in regard to the molecular structure of so-called elements, or in regard to the harmonic relations which may exist between their wave-lengths. Here can be found in juxtaposition the results of various observers upon the metallic spectra of the same metal, and the student can judge of the relative accuracy of the results. A superficial inspection of this Catalogue will show that even distinguished observers, like Thalén and Kirchhoff, often differ in their results by one part in 4000, or one part in 2500. No observer of metallic spectra gives results to more than one tenth of Angström's unit, or to more than one tenth of one wave-length. Physical science, however, now demands a greater degree of Various hypotheses in regard to the apparent coincidences between lines of metallic spectra and lines in the solar spectrum have been propounded, and can only be settled by more accurate measurements of wave-lengths. There are also questions constantly arising in regard to the displacement of lines of spectra due to the motion of the stars and to changes of temperature, which require a greater degree of accuracy in the measurement of wave-lengths of gaseous and metallic spectra than the results of previous observers afford. It may be remarked, that observations upon the metallic spectra of metals from the limits of the visible red to the limits of the visible violet have become comparatively easy; for the solar spectrum can be used to identify the lines of the metals, and to ascertain the wave-lengths. It is only in the extreme infra-red region and in the ultra-violet that such observations become difficult. In these regions we must trust to photography to reproduce, by long exposures of the sensitive plate, the feeble lines of metals which may manifest themselves there. In the infra-red region, as far as wave-length 10,000, it is possible to photograph the solar lines, and we can compare the spectra of such metallic lines as may exist between the A line and the limit 10,000 with the solar spectrum. Beyond this limit, and beyond wave-length 2800 in the violet, the solar spectrum disappears, and the problem of measuring the wave-length of metallic lines which extend beyond these limits becomes a difficult one.

Besides the resolution of the difficulty of measuring the wave-lengths of the invisible rays of light with proper accuracy, the measurement of such wave-lengths is destined to prove a crucial test for various theories which must arise in the progress of physical science. The lines of the metals are exceedingly numerous in the ultra-violet region, far more so

than in the infra-red region. If there are any harmonic relations between the wave-lengths of the spectra of metals, it is here that one might expect to observe such relations. Indeed Professor Grünwald, of Prague, has lately enunciated a remarkable hypothesis upon the relations between the wavelengths of so-called elements, and finds in the observations of various observers in the ultra-violet a strong confirmation of his hypothesis. In any theoretical work upon the grouping of spectral lines, it is of fundamental importance that the wave-lengths of the lines should be determined with as great accuracy as possible. The coincidence of metallic lines with solar lines is at the best a doubtful piece of evidence. evidence is of moment only when the number of coincidences becomes great, and is accompanied by characteristic grouping. A mistake of a wave-length in the question of position is sufficient to destroy the support which the author of any hypothesis might claim for it.

Conditions for Accuracy of Measurement.

All measurements of wave-lengths hitherto published have been made by the old method of angular measurements with a spectrometer. We say old, for the use of Rowland's concave grating with its peculiar mounting must be characterized as a new method and a new departure in measurements of wave-lengths. The observation of wave-lengths of metallic spectra by the eye is most laborious, and the photographic plate must be substituted for the eye for most purposes. The angular positions of the spectral lines on such a plate assume great importance, for upon these positions depend the value of the wave-lengths. In the operation of photographing spectral lines, it is necessary to substitute for the observing-telescope and micrometer-eyepiece of the spectrometer a camera-box provided with a suitable lens, and with a plate-holder for the photographic plate. Unless the latter is small the spectrum will not be in focus on all parts of the plate; moreover, unless the distance of the photographic plate from the diffractiongrating employed is comparatively large, the distances between the spectral lines on the photograph will not be proportional to wave-lengths. To determine these wave-lengths recourse must be had to various devices. The one usually employed is due to Cornu, and can be found described in the Annales de l'Ecole Normale, 2 sér. tome iii. p. 421; also in the Journal de Physique, x. 1881, p. 425. It consists in photographing images of the slit of the spectroscope upon the photographic plate by turning the graduated circle of the spectrometer through measured angles. These photographic images serve

as fiducial marks, by means of which wave-lengths of spectral lines on the plate can be calculated. In the case of diffraction-spectra obtained by deflecting a bundle of parallel rays at the angle of incidence, i, with a deviation of order n,  $\Delta n$  is connected with the wave-length  $\lambda$ , and with a certain constant, a, of the grating by the formula

$$2a\sin\frac{\Delta n}{2}\cos\left(i-\frac{\Delta n}{2}\right)=n\lambda.$$

It is evident that at least two errors can arise in the use of this formula; one from defective graduation of the circle of the spectrometer, another from the process of referring from the photographs of the slit on the plate to the photographs of the metallic lines.

We select the work of Hartley and Adeney\* as perhaps the best type of this method of using a camera with a spectrometer. Their work is characterized by great care and thoroughness, and no one could probably attain better results by the use of a flat grating, with its concomitants of collimator, photographing-lens, and camera. These observers state that they were not troubled by the underlying spectrum of a higher order than that which they photographed, for it was not brought to a focus with the latter. In the new method we propose to illustrate, all the spectra are in focus together, and this fact, instead of being an obstacle, can be turned to great advantage. In the absolute measurements of the wave-length of light, the spectrometer method with eye-observation and with a micrometer is unquestionably more accurate than any photographic method. We have in this determination to deal with comparatively large quantities, and with well-defined directions, which can be made to coincide with optical axes of the instrument; this is not the case, however, with the majority of the spectral lines on a photographic plate placed in the camera, which replaces the observing-telescope of the spectrometer. The photograph contains possible errors, and any shifting or movement of the spectrometer-circle to determine intervals on the photographic plate is apt to introduce other errors.

The ideal arrangement would seem, therefore, to be a photographic apparatus which should remain in focus for all the spectra of the different orders, in which distances between successive lines on the photographs of the spectra should be closely proportional to wave-lengths; so that, the constant being known for a certain position of the sensitive plate, the

<sup>\*</sup> Philosophical Transactions, clxxv. (1884) pp. 63-137.

wave-lengths can be determined by simple linear measurement. Moreover, it is desirable, as we have said, that the underlying spectra should be brought to the same focus as the overlying; for by this means we can compare the wave-lengths of lines in the spectra of different orders, and halve our errors. It is true that some confusion results from having the metallic lines in the spectra of different orders photographed upon the same plate; but a little experience enables one to separate the lines with comparative ease, and the gain in accuracy compensates for the additional trouble.

The apparatus which best answers the requisitions we have pointed out is that of the concave grating of Rowland, with its peculiar mounting, which has been fully described in the

Phil. Mag. [5] vol. xvi. (1883) p. 197.

# Objects of the Present Investigation.

The conclusion of the work of the Committee of the British Association on the tabulation of metallic spectra seemed to us to require a survey of the work, which must be done in the future in order to perfect and correct the work of the past. We have therefore examined the tables given by the committee in order to see what lacunæ could be supplied, and to point out the directions for routine work which may afford material for future generalizations. In the pursuance of this work, we have been compelled to examine the accuracy of measurements of wave-lengths hitherto made in the ultra-With the aid of the new Map of the Solar Spectrum published by Professor Rowland it is very easy to determine the wave-length of metallic lines in the visible spectra of metals; for it is merely necessary to photograph a portion of the solar spectrum upon the same plate as that which receives the spectra of the metals under consideration, and then to refer to the published map. We have already remarked, that even a superficial examination of hitherto published catalogues of wave-lengths of metallic spectra will show that distinguished observers differ in their determinations by one or two wavelengths. The task of remeasuring the wave-lengths of metallic lines is a very great one, and approaches in character the routine work now prosecuted in astronomical observatories in the redetermination of star-places, the photometric intensities of stars, and the classification of star-spectra. In our present work we have confined our attention to ultra-violet spectra. Since the solar spectrum disappears in the neighbourhood of wave-length 2800, the task of identification of wave-lengths becomes a very serious one. To replace the solar spectrum we must refer the lines of metallic spectra to carefully

measured lines of certain metals. When one metal ceases to give spectral lines another must be selected. To test the relative accuracy of what we have termed the old method of measurement with that of the new, we have measured the lines of electrolytic copper, and have compared our results with those of previous observers in regard to the distribution of errors. Besides the comparison of accuracy, we have examined the limit of the spectrum of copper in the ultra-violet, in order to see if that given by previous observers could be extended.

## Apparatus.

The apparatus consisted of a concave grating of 21 ft. 6 in. radius, mounted in the manner described by Professor Rowland. The camera was provided with a shutter, which enabled us to expose different portions of the sensitive plate at pleasure. An alternating dynamo machine was employed, together with a Ruhmkorf coil. The alternating machine gave from eight to ten thousand reversals per second. With a battery of from six to ten two-quart Leyden jars, a powerful spark was obtained between the metallic terminals which we employed. The spark was produced close to the slit of the apparatus, and the time of exposure varied from one to two hours. At various times endeavours were made to substitute the more powerful carbon electric light for the electric spark, in the hope of shortening the time of exposure; but these efforts were not successful. If they had been, we should have been obliged to struggle with the question of impurities in the carbons. An exposure of fifteen minutes to the ultra-violet spectra of metals burned in the electric light produced no image below wave-length 3000. A quartz condensing lens was employed with the arc light, and therefore no light was lost by selective absorption. With the spark no lens was necessary.

By curving the photographic plate all parts of it remain in focus, and distances on the plate are closely proportioned to wave-lengths. If Y = wave-length, we have  $Y = C + \alpha x$ , where C and  $\alpha$  are constants and x is the distance along the

plate.

The determination of the wave-lengths of lines extending over a range of three hundred tenth metres involved the taking of three negatives. The sensitive dry plate  $(2 \times 10)$  inches) was pressed by springs against the "forms" of the plate-holder into an arc of a circle. Having placed the plate-holder on the camera box, the girder bearing the camera and grating was moved along its tracks until the position of

the pointer of the carriage on the scale beside the track indicated that light of wave-lengths 4200 to 4800 in the first spectrum and 2100 to 2400 in the second spectrum would fall on the plate. The shutter was turned so as to expose only the lower half of the plate and a photograph of the solar spectrum from 4200 to 4800 taken. The shutter was again turned, and the upper half of the plate given a long exposure to the light of the spark. Both spectra were in focus. wave-lengths of the metal lines were then found directly, by interpolation on the normal spectrum, from the solar lines whose values were given in Rowland's Photographic Map and table of wave-lengths\*. The interpolation was made by means of measurements on a divided engine. In order to correct for any displacement due to the motion of the spark from side to side, or to jarring arising from the great noise of the spark, and also in order to sift out the lines belonging to the first spectrum from those belonging to the second, the girder was moved to the violet of the third, with its magnified dispersion and different underlying spectra. The metal and solar lines were taken side by side, and the interpolation for the wave-lengths of the metal lines made as before. From this the correction to be applied to the previous plate was found, amounting in some cases to 2 of a tenth metre. correction thus found was applied to all of the lines on the The girder was now moved so that the sensitive plate was in the extreme ultra-violet of the first spectrum, and the plate exposed to the light from the spark. From this negative the values of the wave-lengths of the faint lines were obtained by interpolation from the values of the stronger lines as determined by the first plate. It also served as the final test whether the lines on the first negative were of the first or second order. All of the lines more refrangible than line 2123.1 were in the case of copper found from this negative and from line 2136.1 by direct measurement.

Another method of distinguishing which lines on the first negative belong to the second and which to the first spectrum, is to place in front of the slit while taking the metal lines a piece of plane glass. The second spectrum for this refrangibility will be completely cut out, and only the metal lines of the first remain, being in the visible violet.

The only source of error was in the setting of the microscope upon the broad or faint lines. The probable error of this is about 1 tenth metre. For the few most refrangible

lines it may be greater.

<sup>\*</sup> American Journal of Science, March 1887; Phil. Mag. March 1887.

Effect of Change of Temperature of Source of Light on Constancy of Position of Metallic Lines.

In the progress of the investigation we were much troubled by a slight shifting in position of the metallic lines upon the This shifting could be observed when the photographs. metallic lines were compared with a solar spectrum taken upon the same plate. The amount of this shifting in no case amounted to more than '1 or '2 of a wave-length. At first we thought it might be possible that there was a change in refrangibility of the metallic lines due to a difference in temperature of the source of light, and a long study was made of the influence of the temperature of the source of light upon its wave-length. When a metal was burned in the carbon electric light with varying strength of current, no displacement could be observed between the lines of the metal photographed beneath each other upon the same sensitive plate. When the electric spark with a large battery of Leyden jars was substituted for the electric arc, and the metallic lines obtained by the light of the spark were compared with those from the arc, occasionally a small displacement could be observed. This did not seem to arise from a change of position of the source of light, or from the heating of the slit of the spectroscope. A careful study of the iron lines showed us that the wave-lengths of the iron lines in the sun and those obtained from burning iron in the electric arc were the same to certainly one hundredth of a wave-length. The displacement we observed was noticed only when the electric spark was employed. This shifting did not arise from a change of position of the spark in our apparatus, for it could not be produced at will by changing the position of the source of light. Moreover, when the arc-light was placed in the same position that the spark occupied, no displacement could be observed in photographs taken by the aid of the arc. We were forced to conclude that through the range of temperature afforded by the electric arc and the electric spark the wave-lengths of the metallic lines were constant. The displacement we observed was therefore referred to a jarring of the apparatus due to the noise of the electric spark. When the camera was at a considerable distance from the slit of the spectroscope, the displacement was diminished and sometimes entirely disappeared. The entire apparatus was very solid, and the camera was clamped to a massive girder. It was difficult, therefore, to believe that the displacement could arise from the noise of the spark. We believe, however, that it can be ascribed to this cause, and that the

wave-lengths of metallic lines produced by burning metals in the electric arc or by vaporization in the electric spark are to one hundredth of a wave-length the same as those of the corresponding lines in the sun.

#### Results.

In the following table we have adopted the same symbols and letters to designate the character of the lines which the committee of the British Association have employed. Column 1 refers to the intensity on a scale of 10. Column 2 gives our measurements of the wave-lengths of the copper lines in the ultra-violet, from wave-length 2369.9 to 1944.1. Column 3 contains the measurements of these lines by Hartley and Adeney. Column 4 are the corrections to be applied to Hartley and Adeney's results. Column 5 contains measurements by Liveing and Dewar. Column 6, corrections to be applied to their results. Column 7 gives the symbols adopted by the committee of the British Association, which serve to describe the character of the line:—

1.	2.	3.	4.	5.	6,	7.
Intensity.	Wave- lengths of copper lines. Spark.	Hartley and Adeney.	Corrections.	Liveing and Dewar Arc.	Corrections.	Intensity. B.A.
9 1  4 3 3 1 3  1  7	2369·9 · 2368·8  2356·7 2355·2 2348·8 2346·2 2336·3  2299·6  2294·4 2293·9	2370·1 2368·7 2365·8 2357·2 2355·0 2348·8 2346·2 2336·6 2303·8 2300·5 2297·5 2295·0 2294·6	- ·2 + ·1 - ·5 + ·2 0 - ·3 - ·9 - ·6 - ·7	2294-1	     +3	9 br 2 sd 1 5 sd 2 sd 2 sd 2 sd 1 sd 1 sd 6 sd 3 sd
3 3	2291·1 2286·7	2291·4 2286·7	$\begin{bmatrix} - & 3 \\ - & 3 \\ 0 \\ -1 \cdot 2 \end{bmatrix}$	•••••	···	3 sd 3 sd
6 2	2278·4 2276·3 2265·5 2263·9	2279·6 2277·0 2265·8 2263·9	-1.2 7 3 0	2276·0 2263·6	+·3 +·3	2 sd 6 sd 2 sd 3 nd
7 1 3 3 2 6 2 2 2 2 2 2 2	2263·9 2263·2 2255·1 2249·0	2263·2 2263·2 2257·7 2250·0	$ \begin{array}{c c} 0 \\ -1.6 \\ -1.0 \end{array} $			$egin{array}{c} 3 \ \mathrm{nd} \\ 2 \ \mathrm{sd} \\ 2 \ \mathrm{sd} \end{array}$
7	2247.0	2248·2 2247·7	-1:2	2246.6	+.4	9 sd 3 nd

Table (continued).

1.	2.	3.	4.	5.	6.	7.
Intensity.	Wave- lengths of copper lines. Spark.	Hartley and Adeney.	Corrections.	Liveing and Dewar Arc.	Corrections.	Intensity. B. A.
7	2242.7	2244.0	-1.3	2242.2	+.5	9 sd
	0001.7	2243.5	1.0	•••••	•••	3 nd
1	2231·7 2231·0	2233·0 2232·2	-1·3 -1·2		•••	$\begin{array}{c} 3 \ \mathrm{sd} \\ 3 \ \mathrm{sd} \end{array}$
3	2230.1	2231.2	-1.1	2229.6	+.5	5 sd
$\frac{3}{3}$ $\frac{2}{1}$	2228.9	2230.0	-1:1	2228.3	+.6	5 sd
2	2227.8	2229.1	-1.3			3 sd
	2226.9	2228.1	-1.2	•••••	•••	3 sd
1	2225·7 2224·8	2227.0	-1.3		•••	1 sd
1 6	2218.2	2226.0 $2219.3$	$-1.2 \\ -1.1$	2217.5	+.7	1 sd 6 sd
	22102	2218.5	-11	22110	T	3 nd
2	2215.3	2216.5	-1.2			3 nd
1	2214.4	2215.8	-1.4			3 sd
2 6	2213.0	2214.1	-1.1	0200 7		2 sd
1	2210.3	2211·3 2210·8	-1.0	2209.7	+.6	6  sd 3  nd
		2208.8				2 sd
2	2200.6	2200.3	+ 3			3 sd
2 3	2199.8	2199.8	0	2199.2	+.6	1 nd
3	2196.9	2196.5	+ 4			3 sd
4	2192.4	2192.0	+ 4	2191.8	+.6	6 sd
4	2189.9	2191·2 2189·6	+ '3	2189.2	+.7	3 nd 6 sd
		2188.5				3 nd
1	2181.8	2181.0	+ .8			1 sd
4	2179.5	2179.0	+ .5	2178.8	+.7	5 sd
3	2175.2	2178.0 $2174.5$	+ .7	******		$3  \mathrm{nd}$ $3  \mathrm{sd}$
3	2149.2	2148.8	+ '	2148.9	+.3	3 sd
4	2136.1	2135.8	+ .4	2135.7	+4	3 sd
3 3	2134.6	2134.2	+ 3			2 nd
3	2126.2	2124.4	+ 4			3 sd
3 3	2125·3 2123·1	$\begin{vmatrix} 2124.0 \\ 2122.1 \end{vmatrix}$	+1.8		•••	2 nd
0	21201	2121.5	+1.0		• • • • • • • • • • • • • • • • • • • •	$egin{array}{c} 3  ext{ sd} \ 2  ext{ nd} \end{array}$
3	2117:5	2116.0	7			1 sd
	2112.2	2110.5	+1.5			1 sd
3	2104.9	2103.0	+1.7		• • • •	1 sd
3 2 1	2098.6	1	+1.9			
2	2093·9 2088·1					
2 2 2	2085.5			1		
2	2078.8					
1	2067.0					
1	2062.7					
2 2	2055.1					
2	2045.0	1				

## Table (continued).

	1.	2.	3.	4.	5.	6.	7
I	ntensity.	Wave- lengths of copper lines. Spark.	Hartley and Adeney.	Corrections.	Liveing and Dewar Arc.	Corrections.	Intensity. B.A.
	22 1 1 1 1 2 2 2 1 1	2037·3 2036·0 2030·9 2025·7 2016·9 2015·8 2013·2 1999·9 1989·4 1979·4 1970·4 1944·1					

#### Conclusions.

It will be observed that the corrections to be applied to the wave-lengths obtained by Liveing and Dewar are progressive in their nature when compared with those which must be applied to the results of Hartley and Adeney. difficulty in identifying lines and determining coincidences by employing the tables of metallic spectra in the ultraviolet, published by the British Association, is illustrated by our work; for certain lines measured by Liveing and Dewar, which are identified by the committee with lines given by Hartley and Adeney, are in reality removed from each other, one or two lines intervening. In certain cases the lines of Liveing and Dewar are wholly beyond identification with those given by Hartley and Adeney.

The results of our inquiry into the accuracy of the results of previous observers in measuring wave-lengths of metallic spectra in the ultra-violet can be summed up as follows:—

1. We believe that the method of photographing images of the slit upon the photographic plate, due to Cornu, in order to determine positions, leads to unavoidable errors.

2. The best method of determining wave-lengths of metallic spectra is by the use of concave gratings; for linear measurements are substituted for angular ones, underlying spectra are brought to the same focus as overlying spectra, and, since a great number of lines are in focus on the same plate, the conditions are the same for all, viz. breadth of slit, length of exposure, and source of light.

3. Hypotheses in regard to coincidences of gaseous and metallic spectra cannot be safely based upon existing measure ments of spectra in the ultra-violet.

4. The limit of the copper lines is extended by our investi-

gation.

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# XXXVIII. On Thermoelectric Phenomena. By J. Parker, B.A., late Scholar of St. John's College, Cambridge\*.

WHEN two different metals at the same temperature are put in contact with one another, they assume a difference of potential, and if a current be made to cross the junction, a cooling (or heating) effect is observed. These two facts are evidently dependent on one another, and a relation must exist between them; but though the subject of Thermoelectricity has been frequently considered, a satisfactory explanation appears yet to be found.

Duhem, writing in 1886, says:—"L'analogie des lois qui régissent le phénomène de Peltier avec les lois des différences de niveau potentiel au contact de deux substances différentes a porté certains physiciens à chercher une relation entre ces deux phénomènes, et à regarder le dégagement de chaleur qui correspond au phénomène de Peltier comme proportionnel à la chute que subit la valeur de la fonction potentielle. L'expérience a depuis longtemps démontré que cette propor-

tionnalité n'existait pas."

In this paper a very simple relation is obtained between the Peltier effect and the difference of potential. I have also found the difference of potential and the thermal effect at the junction of two portions of the same metal at different temperatures. Combining these results, we easily find an expression for the electromotive force of a thermo-electric couple, and obtain an analytical proof of the fact, observed by Magnus, that no current is produced by unequal heating in a homogeneous circuit.

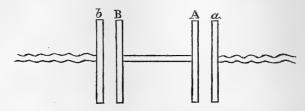
It is well known that when a current crosses a metallic junction kept at a given constant temperature, the heat absorbed (or given out) at the junction depends only on the quantity of electricity that passes, and is independent of the strength of the current.

\* Communicated by the Author.

Take, then, two plates, A, B, of two different metals, say copper and iron, and connect them by a wire of either copper or iron. Parallel and close to these two plates place equal plates of any metal whatever, as zinc, and connect the zinc plates by long zinc wires with a large distant mass of the same metal in the neutral state, so that the zinc plates are constantly at the zero of potential.

Let the mass of the metal A be  $M_{\alpha}$ , its specific heat at constant pressure  $c_{\alpha}$ , its charge  $E_{\alpha}$ , and its potential  $V_{\alpha}$ . Let  $M_{\beta}$ ,  $c_{\beta}$ ,  $E_{\beta}$ ,  $V_{\beta}$  denote similar quantities for the metal B at the same absolute temperature t. Also put  $V_{\beta} - V_{\alpha} = \delta$ .

By a theorem, due originally to Helmholtz, but lately obtained by Duhem as a strict consequence of thermodynamical



principles, the energy of the electrification of the system may be written

$$\frac{1}{2}E_{\alpha}$$
.  $V_{\alpha} + \frac{1}{2}E_{\beta}$ .  $V_{\beta} + E_{\alpha}$ .  $H_{\alpha} + E_{\beta}$ .  $H_{\beta}$ .

As we are only going to consider the case of constant pressure, this may be written

$$\frac{1}{2} \mathbf{E}_{\alpha} \cdot \mathbf{V}_{\alpha} + \frac{1}{2} \mathbf{E}_{\beta} \cdot \mathbf{V}_{\beta} + \mathbf{E}_{\alpha} \cdot f_{\alpha}(t) + \mathbf{E}_{\beta} \cdot f_{\beta}(t)$$
.

Now let our apparatus be made to undergo the following

cycle of reversible operations.

(1) By slowly bringing the plates B nearer together, and slowly separating the plates A, let a quantity of electricity q be made to pass from A to B against the rise of potential  $\delta$  without altering the potential of either A or B. The work done on the system will be

$$-\frac{1}{2}q \cdot \nabla^{\beta} + \frac{1}{2}q \cdot \nabla_{\alpha} = -\frac{1}{2}q\delta.$$

The only thermal effect produced will be at the junction, and the heat *absorbed* there may be represented by  $\Pi$  . q in mechanical units.

Hence

$$\Pi - \frac{1}{2}\delta = \frac{1}{2}(\nabla_{\beta} - \nabla_{\alpha}) + f_{\beta} - f_{\alpha},$$

$$\Pi = \delta + f_{\beta} - f_{\alpha}. \qquad (1)$$

(2) Disconnect the metals A, B, and then raise the temperature to t+dt. The heat absorbed will be

$$(\mathbf{M}_{\alpha}c_{\alpha}+\mathbf{M}_{\beta}c_{\beta})dt+(\mathbf{E}_{\alpha}-q)\frac{df_{\alpha}}{dt}dt+(\mathbf{E}_{\beta}+q)\frac{df_{\beta}}{dt}dt.$$

By slowly moving the plates A and B, let the potentials be altered to  $V_{\alpha}', V_{\beta}'$ , where

$$\nabla_{\beta'} - \nabla_{\alpha'} = \delta + \frac{d\delta}{dt} \cdot dt$$
.

The work done on the system will be

$$\frac{1}{2}(\mathbf{E}_a - q)(\mathbf{V}_a' - \mathbf{V}_a) + \frac{1}{2}(\mathbf{E}_{\beta} + q)(\mathbf{V}_{\beta}' - \mathbf{V}_{\beta}).$$

(3) Connect the plates A and B again, and let q return from B to A without altering the potential of either.

The heat absorbed  $= -(\Pi + d\Pi)q$ , and the work done on

the system  $=\frac{1}{2}q(\delta+d\delta)$ .

(4) Let the plates A, B, be again disconnected, and then reduce the temperature to t. The heat absorbed will be

$$-(\mathbf{M}_{\alpha}c_{\alpha}+\mathbf{M}_{\beta}c_{\beta})dt-\mathbf{E}_{\alpha}\cdot\frac{df_{\alpha}}{dt}dt-\mathbf{E}_{\beta}\cdot\frac{df_{\beta}}{dt}dt.$$

Lastly, bring the potentials back to their original values  $V_a$ ,  $V_{\beta}$ . The work done on the system

$$=\frac{1}{2}E_{\alpha}.(V_{\alpha}-V_{\alpha}')+\frac{1}{2}E_{\beta}.(V_{\beta}-V_{\beta}').$$

The total work done in operations (2) and (4)  $=\frac{1}{2}q \cdot d\delta$ . Hence, from the complete cycle, we have, by the principle of equivalence,

$$-d\Pi \cdot q + q \cdot \left(\frac{\beta}{dt} - \frac{df_a}{dt}\right) dt + q \cdot d\delta = 0,$$

i. e.

$$\frac{d\delta}{dt} = \frac{d\Pi}{dt} - \frac{d}{dt} (f_{\beta} - f_{\alpha}). \qquad (2)$$

Also, by Clausius' principle,

$$\frac{\Pi}{t} - \frac{\Pi + d\Pi}{t + dt} + \frac{1}{t} \left( \frac{df_{\beta}}{dt} - \frac{df_{\alpha}}{dt} \right) dt = 0,$$

i. e.

$$\frac{d}{dt}\left(\frac{\Pi}{t}\right) = \frac{1}{t} \frac{d}{dt} (f_{\beta} - f_{\alpha}). \qquad (3)$$

Hence, by (2) and (3),

$$\Pi = t \frac{d\delta}{dt}. \qquad (4)$$

Also we have seen that

$$\Pi = \delta + f_{\beta} - f_{\alpha}$$
;

therefore

$$\frac{d}{dt}\left(\frac{\delta}{t}\right) = \frac{f_{\beta} - f_{a}}{t^{2}}. \quad . \quad . \quad . \quad . \quad (5)$$

Equations (4) and (5) contain the whole theory of the Peltier effect and the difference of potential.

Let us now consider the case of two portions of the same

metal at different temperatures.

Let the quantities  $\dot{\mathbf{M}}$ , c,  $\mathbf{E}$ ,  $\mathbf{V}$ , refer to a portion at the absolute temperature t, and let  $\mathbf{M}_1$ ,  $c_1$ ,  $\mathbf{E}_1$ ,  $\mathbf{V}_1$ , refer to another portion at temperature  $t_1$ , where  $t_1 = t + \tau$ ,  $\tau$  being indefinitely small. Also suppose the system to undergo the following cycle of operations.

(1) Let a quantity of electricity, q, be made to pass from M to  $M_1$  without altering the potential of either. The work

done on the system will be

$$\frac{1}{2}q(\mathbf{V}-\mathbf{V}_1) \equiv -\frac{1}{2}q\frac{d\mathbf{V}}{dt}$$
.  $\tau$ .

The heat absorbed at the junction may be represented by  $\sigma\tau$ . q. The increase of the energy of the system will be

$$\frac{1}{2}q(\mathbf{V}_1-\mathbf{V})+q\left\{f(t_1)-f(t)\right\} = \frac{1}{2}q\frac{d\mathbf{V}}{dt}\tau+q\frac{df}{dt}\tau.$$

Hence

$$\sigma - \frac{1}{2} \cdot \frac{dV}{dt} = \frac{1}{2} \frac{dV}{dt} + \frac{df}{dt};$$

$$\sigma = \frac{dV}{dt} + \frac{df}{dt}. \qquad (6)$$

therefore

(2) Separate M and  $M_1$ , and then raise the temperature of each by  $\theta$ . The increase of entropy will be

$$\begin{split} \mathbf{M}c \int_{t}^{t+\theta} \frac{dt}{t} + \mathbf{M}_{1}c_{1} \int_{t_{1}}^{t_{1}+\theta} \frac{dt}{t} + (\mathbf{E} - q) \int_{t}^{t+\theta} \frac{1}{t} \frac{df}{dt} \, dt \\ + (\mathbf{E}_{1} + q) \int_{t_{1}}^{t_{1}+\theta} \frac{1}{t} \frac{df}{dt} \, dt. \end{split}$$

(3) After reducing M and M<sub>1</sub> to a state of electric equilibrium, which may be done without producing any thermal

effect, make q return from  $M_1$  to M without altering the potential of either. The heat absorbed at the junction may be written

$$-\sigma'\tau q.$$

(4) Again disconnect M and  $M_1$ , and then reduce their temperatures to their original values. The increase of entropy will be

$$\begin{split} -\mathbf{M}c \int_{t}^{t+\theta} \frac{dt}{t} - \mathbf{M}_{1}c_{1} \int_{t_{1}}^{t_{1}+\theta} \frac{dt}{t} - \mathbf{E} \cdot \int_{t}^{t+\theta} \frac{1}{t} \frac{df}{dt} dt \\ - \mathbf{E}_{1} \cdot \int_{t_{1}}^{t_{1}+\theta} \frac{1}{t} \frac{df}{dt} dt. \end{split}$$

Lastly, reduce the potentials to their original values V, V<sub>1</sub>, which may be done without producing any thermal effect.

If we can apply Carnot's principle to the cycle just described, we get

$$\tau\left(\frac{\sigma}{t} - \frac{\sigma'}{t+\theta}\right) - \int_{t}^{t+\theta} \frac{1}{t} \frac{df}{dt} dt + \int_{t_{1}}^{t_{1}+\theta} \frac{1}{t} \frac{df}{dt} dt = 0 ;$$
i. e.
$$\tau\left(\frac{\sigma}{t} - \frac{\sigma'}{t+\theta}\right) - \int_{t}^{t_{1}} \frac{1}{t} \frac{df}{dt} dt + \int_{t+\theta}^{t_{1}+\theta} \frac{1}{t} \frac{df}{dt} dt = 0 ;$$
i. e.
$$\frac{\sigma}{t} - \frac{\sigma'}{t+\theta} + \frac{1}{t+\theta} \frac{df(t+\theta)}{d(t+\theta)} - \frac{1}{t} \frac{df}{dt} = 0.$$

Hence  $\frac{\sigma}{t} - \frac{1}{t} \frac{df}{dt}$  is independent of t, and =k, say.

Hence, by (6), 
$$\frac{d\mathbf{V}}{dt} = kt.$$

If, now, we join two portions of the same metal, whose temperatures t,  $t_0$  differ by a finite amount, and if V,  $V_0$  be the potentials which they assume, then

$$V - V_0 = \frac{1}{2}k \cdot (t^2 - t_0^2) = \Delta$$
, say. . . . (7)

Also, if S. q be the heat absorbed at the junction when a quantity of electricity q passes from  $t_0$  to t,

$$S = \frac{1}{2} k \cdot (t^2 - t_0^2) + f(t) - f(t_0) = \Delta + f(t) - f(t_0). \quad . \quad (8)$$

It follows immediately from (7) that if we take a piece of homogeneous wire unequally heated, the difference of the potentials of the two ends will be the same as if they were actually in contact. The ends of the wire may therefore be

joined so as to form a circuit without disturbing the equilibrium, as Magnus long ago found by experiment.

Again, let A, B be two pieces of different metals in contact,



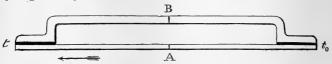
and let the temperature at the junction be t, and the difference of potential  $\delta$ . Then, if the free ends be at the same temperature  $t_0$ , their potentials will differ by

$$\frac{1}{2}k_{\beta}(t_0^2-t^2)+\delta+\frac{1}{2}k_{\alpha}(t^2-t_0^2).$$

This is not generally equal to  $\delta_0$ , and therefore, if the ends be

joined, a current will be produced.

Let us now make a thermoelectric circuit of the two metals A, B, and keep the junctions at the absolute temperatures t,  $t_0$  respectively.



Let R be the resistance of the circuit, and J the intensity of the current, supposed to flow from A to B through the junction of temperature t.

The "electromotive force" of the circuit is defined to be

 $\mathbf{E} = \mathbf{RJ}.$ 

The heat generated in the homogeneous parts of the circuit will be, by Joule's law, RJ<sup>2</sup> in a unit of time. This is exactly balanced by the heat absorbed at the junctions, which in a unit of time is equal to

$$J.(\Pi - \Pi_0 + S - S_\beta).$$

Hence

$$E = \Pi - \Pi_0 + S_{\alpha} - S_{\beta}$$
  
=  $\delta - \delta_0 + \Delta_{\alpha} - \Delta_{\beta}$ , . . . . . (9)

by equations (1) and (8).

It is à priori evident that the fall of potential in the homogeneous parts of the circuit must be exactly compensated by the abrupt rises of potential at the junctions, so that equation (9) affords a partial verification of our theory.

If the temperatures t,  $t_0$  differ by an infinitesimal quantity

7, the electromotive force takes the form

$$\left\{\frac{\Pi}{t} + (k_{\alpha} - k^{\beta}) \cdot t\right\} \cdot \tau. \quad . \quad . \quad (10)$$

Now suppose that when one junction is maintained at a

certain temperature T, the current flows through the circuit in the same direction whether the other junction be hotter or colder; then

 $\Pi = (k_{\beta} - k_{\alpha}) \cdot \mathrm{T}^2;$ 

so that the Peltier effect does not then cease, as is commonly supposed.

Again, by (9),

$$\frac{d\Pi}{dt} + \sigma_{\alpha} - \sigma_{\beta} = \frac{d\delta}{dt} + (k_{\alpha} - k_{\beta})t.$$

Hence, by (4),

$$t \frac{d}{dt} \left( \frac{\Pi}{t} \right) + \sigma_{\alpha} - \sigma_{\beta} = (k_{\alpha} - k_{\beta})t.$$

If the "specific heats" of electricity in the two metals are proportional to the absolute temperature, so that  $\sigma_{\alpha} = l_{\alpha}t$ ,  $\sigma_{\beta} = l_{\beta}t$ , we have

$$\frac{d}{dt}\left(\frac{\Pi}{t}\right) = (k_{\alpha} - l_{\alpha}) - (k_{\beta} - l_{\beta}).$$

Therefore

$$\Pi = \{ (k_{\alpha} - l_{\alpha}) - (k_{\beta} - l_{\beta}) \} t^{2} + Ct, 
\delta = \frac{1}{2} \{ (k_{\alpha} - l_{\alpha}) - (k_{\beta} - l_{\beta}) \} t^{2} + Ct + C',$$
(11)

where C, C' are independent of t.

Now

$$\Pi = (k_{\beta} - k_{\alpha})T^2$$
 when  $t = T$ ;

therefore

C+ 
$$\{(2k_{\alpha}-l_{\alpha})-(2k_{\beta}-l_{\beta})\}$$
T=0. . . (12)

Thus, by (9), the electromotive force of the circuit becomes

$$\mathbf{E} = \left\{ \left( k_{\alpha} - \frac{l}{2} \right) - \left( k_{\beta} - \frac{l_{\beta}}{2} \right) \right\} (t^{2} - t_{0}^{2}) + \mathbf{C}(t - t_{0})$$

$$= -\frac{\mathbf{C}}{2\mathbf{T}} (t^{2} - t_{0}^{2}) + \mathbf{C}(t - t_{0}) \dots \text{ by (12)}$$

$$= \frac{\mathbf{C}}{\mathbf{T}} (t - t_{0}) \left\{ \mathbf{T} - \frac{t + t_{0}}{2} \right\}, \dots \dots \dots \dots (13)$$

a formula first obtained by Prof. Tait.

Also

$$\frac{f_{\beta} - f_{\alpha}}{t^{2}} = \frac{d}{dt} \left( \frac{\delta}{t} \right) \dots \text{ by (5)}$$

$$= \frac{1}{2} \left\{ (k_{\alpha} - l_{\alpha}) - (k_{\beta} - l_{\beta}) \right\} - \frac{C'}{t^{2}} \dots \text{ by (11)},$$

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and therefore

$$f_{\beta}(t) = -\frac{1}{2} (k_{\beta} - l_{\beta}) t^{2} + C_{\beta},$$

$$f_{\alpha}(t) = -\frac{1}{2} (k_{\alpha} - l_{\alpha}) t^{2} + C_{\alpha},$$
(14)

where  $C_a$ ,  $C_{\beta}$  are constants such that

$$C' + C_{\beta} - C_{\alpha} = 0.$$

XXXIX. On Electromagnetic Waves, especially in relation to the Vorticity of the Impressed Forces; and the Forced Vibrations of Electromagnetic Systems. By OLIVER HEAVISIDE.

[Continued from vol. xxv. p. 405.]

31. SPHERICAL Waves (with diffusion) in a Conducting Dielectric.—In an infinitely extended homogeneous isotropic conducting dielectric, let the surface r=a be a sheet of vorticity of impressed electric force; for simplicity, let it be of the first order, so that the surface-density is represented by  $f\nu$ . By (127), § 20, the differential equation of H, the intensity of magnetic force is, at distance r from the origin, outside the surface of f ( $\nu$  meaning  $\sin \theta$ ),

$$\mathbf{H} = \frac{k_1}{q} \left( \frac{\nu a}{r} \right) \epsilon^{-qr} \left( 1 + \frac{1}{qr} \right) \left\{ \cosh qa - \frac{\sinh qa}{qa} \right\} f, \quad (206)$$

where f may be any function of the time. Here, in the general case, including the unreal "magnetic conductivity" g,\* we have

$$q = [(4\pi k + cp)(4\pi g + \mu p)]^{\frac{1}{2}} = v^{-1}[(p+\rho)^2 - \sigma^2]^{\frac{1}{2}},$$

$$k_1 = 4\pi k + cp;$$
(207)

if, for subsequent convenience,

$$\rho_1 = 4\pi k/2c, \quad \rho_2 = 4\pi g/2\mu, \quad v = (\mu c)^{-\frac{1}{2}}; \\ \rho = \rho_1 + \rho_2, \quad \sigma = \rho_1 - \rho_2.$$
 (208)

The speed is v, and  $\rho_1$ ,  $\rho_2$  are the coefficients of attenuation of the parts transmitted of elementary disturbances due to the real electric conductivity k and the unreal g; that is,  $\epsilon^{-\rho t}$  is the factor of attenuation due to conductivity. On the

<sup>\*</sup> Owing to the lapse of time, I should mention that the physical and other meanings of the coefficient g are explained in the first part of this Paper, Phil. Mag. Feb. 1888. Also k= electric conductivity;  $\mu$ = magnetic inductivity; and  $c/4\pi$  = electric permittivity. All the problems in this paper, except in § 43, relate to spherical waves; the geometrical coordinates are r and  $\theta$ . Unless otherwise mentioned, p always signifies the operator d/dt, t being the time.

other hand, the distortion produced by conductivity depends on  $\sigma$ , and vanishes with it. There is some utility in keeping in g, because it sometimes happens that the vanishing of k, making  $\rho = -\sigma$ , leads to a solvable case. We can then produce a real problem by changing the meaning of the symbols, turning the magnetic into an electric field, with other changes

to correspond.

32. The steady Magnetic Field due to f constant.—Let f be zero before, and constant after t=0, the whole medium having been previously free from electric and magnetic force. All subsequent disturbances are entirely due to f. The steady field which finally results is expressed by (206), by taking p=0; that is,  $k_1$  has to mean  $4\pi k$ , and  $q=4\pi (kg)^{\frac{1}{2}}$ , by (207). To obtain the corresponding internal field, exchange a and r in (206), except in the first a/r. The same values of  $k_1$  and q used in the corresponding equations of E and F give the final electric field. The steady magnetic field here considered

depends upon g, and vanishes with it.

33. Variable state when  $\rho_1 = \rho_2$ . First case. Subsiding f.— There are cases in which we already know how the final state is reached, viz. the already given case of a nonconducting dielectric (§§ 21, 22), and the case  $\sigma=0$  in (208), which is an example of the theory of § 4. In the latter case the impressed force must subside at the same rate as do the disturbances it sends out from the surface of f. Thus, given  $f=f_0e^{-\rho t}$ , starting when t=0, with  $f_0$  constant, the resulting electric and magnetic fields are represented by those in the corresponding case in a nonconducting dielectric, when multiplied by  $e^{-\rho t}$ . The final state is zero because f subsides to zero; the travelling shell also loses all its energy. But there are, in a sense, two final states; the first commencing at any place as soon as the rear of the travelling shell reaches it, and which is entirely an electric field; the second is zero, produced by the subsidence of this electric field. There is no magnetic field to correspond, and therefore no "true" electric current, in Maxwell's sense of the term, except in the shell.

34. Second case. f constant.—But let the impressed f be constant. Then, by effecting the integrations in (206), we

are immediately led to the full solution

$$\begin{split} \mathbf{H} &= \frac{f \nu a}{2 \mu v r} \left[ \epsilon^{-\frac{\rho}{v}(r-a)} \left( 1 + \frac{v}{\rho r} \right) \left( 1 - \frac{v}{\rho a} \right) + \epsilon^{-\rho t} (1 + \rho t) \frac{v^2}{r a \rho^2} \right. \\ &\quad + \text{ same function of } -a \right], \quad . \quad . \quad (209) \end{split}$$

where the fully represented part expresses the primary wave out from the surface of f, reaching r at time (r-a)/v; whilst

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the rest expresses the second wave, reaching r when t = (r+a)/v. After that the actual H is their sum, viz.

$$H = \frac{f v a}{\mu v r} e^{-\rho r/v} \left( 1 + \frac{v}{\rho r} \right) \left[ \cosh - \frac{v}{\rho a} \sinh \right] \frac{\rho a}{v}, \quad (210)$$

agreeing with (206), when we give q therein the special value  $\rho/v$  at present concerned, and  $k_1 = 4\pi k$ .

At the front of the first wave we have

$$\mathbf{H} = e^{-\rho t} f va/2\mu vr, \quad . \quad . \quad . \quad . \quad (211)$$

so that the energy in the travelling shell still subsides to zero. Equation (211) also expresses H at the front of the inward wave, both before and after reaching the centre of the sphere. The exchange of a and r in the [] in (209) produces the corresponding internal solution.

35. Unequal  $\rho_1$  and  $\rho_2$ . General case.—If we put  $d/dr = \nabla$ ,

we may write (206) thus,

$$\mathbf{H} = \frac{\nu a}{2r} \frac{k_1}{q^3} \left[ \left( \nabla - \frac{1}{r} \right) \left( \nabla + \frac{1}{a} \right) e^{-q(r-a)} + \left( \nabla - \frac{1}{r} \right) \left( \nabla - \frac{1}{a} \right) e^{-q(r+a)} \right] f. \quad (212)$$

It is, therefore, sufficient to find

$$\epsilon^{-q(r-a)}q^{-3}f$$
, . . . . . (213)

to obtain the complete solution of (212); namely, by performing upon the solution (213) the differentiations  $\nabla$  and the operation  $k_1$ . This refers to the first half of (212); the second half only requires the sign of a to be changed in the  $\lceil \rceil$ .

Now (213) is the same as

$$v^3 e^{-\rho t} e^{-\frac{r-a}{v}(p^2-\sigma^2)^{\frac{1}{2}}} (p^2-\sigma^2)^{-\frac{3}{2}} (f e^{\rho t}).$$
 (214)

Expand the two functions of p in descending powers of p, thus,

$$(p^{2}-\sigma^{2})^{-\frac{3}{2}} = p^{-3} \left[ 1 + \frac{3}{2} \frac{\sigma^{2}}{p^{2}} + \frac{3 \cdot 5}{2^{2} | 2} \frac{\sigma^{4}}{p^{4}} + \frac{3 \cdot 5 \cdot 7}{2^{3} | 3} \frac{\sigma^{6}}{p^{6}} + \dots \right], (215)$$

$$\epsilon^{-\frac{r-a}{v}(p^2-\sigma^2)^{\frac{1}{2}}} = \epsilon^{-\frac{p}{v}(r-a)} \left[ 1 + \frac{\sigma}{p} h_1 + \frac{\sigma^2}{p^2} h_2 + \dots \right], \quad . \quad . \quad (216)$$

where the h's are functions of r, but not of p. Multiplying these together, we convert (213) or (214) to

$$v^3 e^{-\rho t} e^{-\frac{p}{v}(r-a)} \frac{1}{p^3} \left[ 1 + \frac{\sigma}{p} i_1 + \frac{\sigma^2}{p^2} i_2 + \dots \right] (fe^{\rho t}), \quad (217)$$

where the i's are functions of r, but not of p. The integrations can now be effected. Let f be constant, first. Then.

f starting when t=0, we have

$$p^{-3}(f\epsilon^{\rho t}) = f\rho^{-3}(\epsilon^{\rho t} - 1 - \rho t - \frac{1}{2}\rho^2 t^2) = \rho^{-3}f(\epsilon^{\rho t})_3 \text{ say};$$
 (218)

&c. &c. Next, operating with the exponential containing p in (217) turns t to t-(r-a)/v, and gives the required solution in the form

$$\begin{split} \mathbf{H} = & \frac{fvav^2}{2\mu vr} \, \epsilon^{-\rho t} (\sigma + p) \, \Big[ \Big( \nabla - \frac{1}{r} \Big) \Big( \nabla + \frac{1}{a} \Big) \, \Big\{ \frac{(\epsilon^{\rho t_1})_3}{\rho^3} + \sigma i_1 \, \frac{(\epsilon^{\rho t_1})_4}{\rho^4} + \dots \, \Big\} \\ & + \text{ same function of } -a \, \Big], \quad (219) \end{split}$$

where  $t_1=t-(r-a)/v$ ; the represented part beginning when  $t_1$  reaches zero, and the rest when t-(r+a)/v reaches zero.

36. Fuller development in a special case. Theorems involving Irrational Operators.—As this process is very complex, and (219) does not admit of being brought to a readily interpretable form, we should seek for special cases which are, when fully developed, of a comparatively simple nature. Write the first half of (212) thus,

$$\mathbf{H} = \frac{cv^3 \nu a}{2r} \, \epsilon^{-\rho t} \left( \nabla - \frac{1}{r} \right) \left( \nabla + \frac{1}{a} \right) \frac{1}{p^2 - \sigma^2} \left[ \left( \frac{p + \sigma}{p - \sigma} \right)^{\frac{1}{2}} \epsilon^{-\frac{r - a}{v} (p^2 - \sigma^2)^{\frac{1}{2}}} (f \epsilon^{\rho t}) \right]. \tag{220}$$

Now the part in the square brackets can be finitely integrated when  $fe^{\rho t}$  subsides in a certain way. We can show that

$$\binom{p+\sigma}{p-\sigma}^{\frac{1}{2}} e^{-\frac{r-a}{v}(p^2-\sigma^2)^{\frac{1}{2}}} (e^{-\sigma t}) = J_0 \left\{ \frac{\sigma}{v} \left[ (r-a)^2 - v^2 t^2 \right]^{\frac{1}{2}} \right\}, (221)$$

in which, observe, the sign of  $\sigma$  may be changed, making no difference on the right side (the result), but a great deal on the left side.

The simplest proof of (221) is perhaps this. First let r=a. Then

$$\left(\frac{p+\sigma}{p-\sigma}\right)^{\frac{1}{2}}(\epsilon^{-\sigma t}) = \epsilon^{-\sigma t} \left(1 - \frac{2\sigma}{p}\right)^{-\frac{1}{2}}(1), \quad . \quad (222)$$

by getting the exponential to the left side, so as to operate on unity. Next, by the binomial theorem,

$$= \epsilon^{-\sigma t} \left[ 1 + \frac{1}{2} \frac{2\sigma}{p} + \frac{1 \cdot 3}{2^2 | 2} \left( \frac{2\sigma}{p} \right)^2 + \dots \right] (1). \quad (223)$$

Now integrate, and we have (f commencing when t=0),

$$= \epsilon^{-\sigma t} \left( 1 + \sigma t + \frac{1 \cdot 3}{|2|^2} \sigma^2 t^2 + \frac{1 \cdot 3 \cdot 5}{|3|^3} \sigma^3 t^3 + \cdots \right),$$

$$= \epsilon^{-\sigma t} \epsilon^{\sigma t} J_0(\sigma t i) ;$$
(224)

364 Mr. O. Heaviside on Electromagnetic Waves, and the so that, finally,

 $\left(\frac{p+\sigma}{p-\sigma}\right)^{\frac{1}{2}}(\epsilon^{-\sigma t}) = \mathbf{J}_0(\sigma t i). \qquad (225)$ 

It is also worth notice that, integrating in a similar manner,

These theorems present themselves naturally in problems relating to a telegraph-circuit, when treated by the method of resistance-operators. A special case of (225) is

$$p^{\frac{1}{2}}(1) = (\pi t)^{-\frac{1}{2}}, \qquad (227)$$

which presents itself in the electrostatic theory of a submarine\* cable.

We have now to generalize (225) to meet the case (221). The left member of (221) satisfies the partial differential equation

$$v^2 \nabla^2 = p^2 - \sigma^2$$
, . . . . (228)

so we have to find the solution of (228) which becomes  $J_0(\sigma ti)$  when r=a. Physical considerations show that it must be an even function of (r-a), so that it is suggested that the t in  $J_0$  ( $\sigma ti$ ) has to become, not t-(r-a)/v or t+(r-a)/v, but that  $t^2$  has to become their product. In any case, the right member of (221) does satisfy (228) and the further prescribed condition, so that (221) is correct.

\* Thus, let an infinitely long circuit, with constants R, S, K, L, be operated upon by impressed force at the place z=0, producing the potential-difference  $V_0$  there, which may be any function of the time. Let C be the current and V the potential-difference at time t at distance x. Then

$$C = \left(\frac{K + Sp}{R + Lp}\right)^{\frac{1}{2}} \epsilon^{-qz} V_0,$$

where  $q=(\mathbf{R}+\mathbf{L}p)^{\frac{1}{2}}(\mathbf{K}+\mathbf{S}p)^{\frac{1}{2}}$ . Take  $\mathbf{K}=0$ , and  $\mathbf{L}=0$ ; then, if  $\mathbf{V}_0$  be zero before and constant after t=0, the current at z=0 is given by

$$C_0 = V_0 (S/R)^{\frac{1}{2}} p^{\frac{1}{2}} (1),$$

and (227) gives the solution. Prove thus: let b be any constant, to be finally made infinite; then

$$\begin{array}{l} p^{\frac{1}{2}}(1) = b^{\frac{1}{2}}(1 + bp^{-1})^{-\frac{1}{2}} \\ = b^{\frac{1}{2}}\mathbf{J}_{0}(\frac{1}{2}bti)\epsilon^{-bt/2} \end{array}$$

by the investigation in the text. Now put  $b=\infty$ , and (227) results. In the similar treatment of cylindrical waves in a conductor,  $p_1^*$ ,  $p_2^*$ , &c. occur. We may express these results in terms of Gamma functions.

If a direct proof be required, expand the exponential operator in (221) containing r in the way indicated in (216), and let the result operate upon  $J_0(\sigma ti)$ . The integrated result can

be simplified down to (221).

37. Now use (221) in (220). Let  $fe^{\rho t} = f_0 e^{-\sigma t}$ , where  $f_0$  is constant; and the square bracket in (220) becomes known, being in fact the right member of (221) multiplied by  $f_0$ . So, making use also of (228), we bring (220) to

$$\mathbf{H} = \frac{vaf_0}{2\mu vr} e^{-\rho t} \left[ 1 + \left\{ \left( \frac{1}{a} - \frac{1}{r} \right) v^2 \frac{d}{dr} - \frac{v^2}{ar} \right\} \frac{1}{p^2 - \sigma^2} \right]$$

$$\mathbf{J}_0 \left\{ \frac{\sigma}{v} \left[ (r - a)^2 - v^2 t^2 \right]^{\frac{1}{2}} \right\}; (229)$$

to which must be added the other part, beginning 2a/v later, got by negativing a, except the first one. The operation  $(p^2 - \sigma^2)^{-1}$  may be replaced by two integrations with respect to r.

Let r and a be infinitely great, thus abolishing the curvature. Let r-a=z, and  $f_0\nu a/r$ , which is now constant, be called  $e_0$ . Then we have simply

$$\mathbf{H} = \frac{e_0}{2\mu v} \mathbf{e}^{-\rho t} \, \mathbf{J}_0 \left\{ \frac{\sigma}{v} \left( z^2 - v^2 t^2 \right)^{\frac{1}{2}} \right\}, \quad . \quad . \quad (230)$$

showing the H produced in an infinite homogeneous conducting dielectric medium at time t after the introduction of a plane sheet (at z=0), of vorticity of impressed electric force, the surface density of vorticity being  $e_0e^{-2\rho_1t}$ . This corroborates the solution in § 8, equation (51) (vol. xxv. p. 140), whilst somewhat extending its meaning.

The condition to which f is subject may be written, by

(208),

$$f = f_0 e^{-2\rho_1 t}, \dots (231)$$

where  $f_0$  is constant. If, then, we desire f to be constant,  $\rho_1$  must vanish, which, by (208), requires k=0, whilst g may be finite.

But we can make the problem real thus. In (229) change H to E and  $\mu\nu$  to cv; we have now the solution of the problem of finding the electric field produced by suddenly magnetizing uniformly a spherical portion of a conducting dielectric; i.e. the vorticity of the impressed magnetic force is to be on the surface of the sphere r=a, parallel to its lines of latitude, and of surface-density  $f\nu$ , such that  $f\nu e^{2\rho_2 t}$  is constant. This makes f constant when g=0 and k finite, representing a real conducting dielectric.

38. The electric force at the origin due to fv at r=a.—Returning to the case of impressed electric force, the differential equation of F, the radial component of electric force inside the sphere on whose surface r=a the vorticity of e is situated, is, by § 21,

$$\mathbf{F} = \frac{2a \cos \theta}{qr^2} \epsilon^{qa} \left(1 + \frac{1}{qa}\right) \left(\cosh qr - \frac{\sinh qr}{qr}\right) f, (232)$$

At the centre, therefore, the intensity of the full force, which call  $F_0$ , whose direction is parallel to the axis, is

$$F_0 = \frac{2}{3}(1+qa)\epsilon^{-qa}f = \frac{2}{3}\left(1-a\frac{d}{da}\right)\epsilon^{-qa}f.$$
 (233)

Unless otherwise specified, I may repeat that the forces referred to are always those of the fluxes, thus doing away with any consideration of the distribution of the impressed force, and of scalar potential, of varying form, which it involves. (233) is equivalent to

$$F_0 = \frac{2}{3} e^{-\rho t} \left\{ 1 + av^{-1} \left( p^2 - \sigma^2 \right)^{\frac{1}{2}} \right\} e^{-av^{-1}(p^2 - \sigma^2)^{\frac{1}{2}}} (fe^{\rho t}) . \quad (234)$$

Let f be constant, and  $\rho = \sigma$ , or g = 0. Then (234) becomes

$$\mathbf{F}_0 = \frac{2}{3} f e^{-\sigma t} \left[ \frac{a}{v} (p+\sigma) \left( \frac{p-\sigma}{p+\sigma} \right)^{\frac{1}{2}} + 1 \right] e^{-a^{v-1} (p^2-\sigma^2)^{\frac{1}{2}}} (e^{\sigma t}), \quad (235)$$

of which the complete solution is, by (221),

$$\begin{split} \mathbf{F}_0 = & (\frac{2}{3}f) \left[ e^{-\sigma t} a v^{-1} (p+\sigma) \mathbf{J}_0 \{ \sigma v^{-1} (a^2 - v^2 t^2)^{\frac{1}{2}} \} + \mathbf{X}_a \right], \ \ (236) \end{split}$$
 where, subject to g = 0,

$$\epsilon^{-qa}(1) = X_a; \ldots (236a)$$

or, solved,

$$X_{a} = 1 - e^{-\sigma t} \left[ \frac{\sigma^{a}}{v} \left( J_{0} + \frac{J_{1}}{i} \right) - \frac{1}{\underline{|3}} \left( \frac{\sigma^{a}}{v} \right)^{3} \frac{1}{\sigma t} \left( \frac{J_{1}}{i} + \frac{J_{2}}{i^{2}} \right) + \frac{1 \cdot 3}{\underline{|5|}} \left( \frac{\sigma^{a}}{v} \right)^{5} \frac{1}{\sigma^{2} t^{2}} \left( \frac{J_{2}}{i^{2}} + \frac{J_{3}}{i^{3}} \right) - \dots \right], \quad (237)$$

in which  $i=(-1)^{\frac{1}{2}}$ , and all the J's operate upon  $\sigma ti$ . This solution (236) begins when t=a/v. The value of  $\sigma$  is  $4\pi k/2c$ .

In a good conductor  $\sigma$  is immense. Then assume c=0, or do away with the elastic displacement, and reduce (236) to the pure diffusion formula, which is

$$\mathbf{F}_{0} = \left(\frac{2}{3}f\right) \left[ \left(\frac{2}{\pi}\right)^{\frac{1}{2}} y e^{-\frac{1}{2}y^{2}} + 1 - \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \left\{ y - \frac{y^{3}}{|3|} + \frac{1 \cdot 3}{|5|} y^{5} - \dots \right\} \right], (238)$$

where  $y = (4\pi\mu ka^2/2t)^{\frac{1}{2}}$ . The relation of  $X_a$  in (236) to the preceding terms is explained by equations (233) or (235).

39. Effect of uniformly magnetizing a Conducting Sphere surrounded by a Nonconducting Dielectric.—Here, of course, it is the lines of **E** that are circles centred upon the axis, both inside and outside. Let **h** be the impressed magnetic force, and  $h\nu$  the surface-density of its vorticity, at r=a, outside which the medium is nonconducting, and inside a conducting dielectric. The differential equation of  $E_a$ , the surface value of the tensor of **E** at r=a, is [compare (124), § 19]

$$\frac{h\nu}{E_a} = \left(\frac{1}{\mu p} \frac{W'}{W}\right)_{\text{out}} - \left(\frac{1}{\mu p} \frac{U' + W'}{U + W}\right)_{\text{in}}; \quad (239)$$

in which r=a, and  $\mu$  and q are to have the proper values on the two sides of the surface.

Now, by (111),

$$W'/W = -q\{1+(qr)^{-1}(1+qr)^{-1}\}$$
. (240)

in the case of m=1, (first order), here considered. This refers to the external dielectric, in which q=p/v. Let  $v=\infty$ , making

This assumption is justifiable when the sphere has sensible conductivity, on account of the slowness of action it creates in comparison with the rapidity of propagation in the dielectric outside. Then (239) becomes,

$$-\frac{h\nu}{\mathbf{E}_a} = \frac{1}{\mu_1 p a} \frac{q_1 a \sinh q_1 a}{\cosh q_1 a - (q_1 a)^{-1} \sinh q_1 a} + \frac{1}{p a} \left(\frac{1}{\mu_0} - \frac{1}{\mu_1}\right), (242)$$

if  $\mu_0$  is the external and  $\mu_1$  the internal inductivity, and  $q_1$  the internal q. When the inductivities are equal, there is a material simplification, leading to

$$\mathbf{E}_{a} = -\mu p a \frac{\cosh q_{1} a - (q_{1} a)^{-1} \sinh q_{1} a}{q_{1} a \sinh q_{1} a} h \nu, \quad . \quad (243)$$

where  $q_1 = \{(4\pi k_1 + c_1 p)\mu_1 p\}_{\frac{1}{2}}$ . First let  $c_1 = 0$ , in the conductor, making  $q_1^2 = 4\pi \mu_1 k_1 p = -s^2$ , say. Then

$$\mathbf{E}_{a} = -\frac{1}{4\pi k_{1}a} \frac{\cos sa - (sa)^{-1} \sin sa}{(sa)^{-1} \sin sa} h\nu. \quad . \quad (244)$$

From this we see that  $\sin sa = 0$  is the determinantal equation of normal systems. The slowest is

$$sa = \pi$$
, or  $-p^{-1} = 4\mu_1 k_1 a^2 / \pi$ . . . (245)

This time-constant is about  $(1250)^{-1}$  second if the sphere be of copper of 1 centim. radius; about 8 seconds if of 1 metre radius, and about 10 million years if of the size of the earth.

At distance r from the centre of the sphere, within it, at time t after starting h, we have

$$E = -\frac{h\nu}{4\pi k_1 r} \sum_{r} \frac{\cos sr - (sr)^{-1} \sin sr}{p(d/dp)\{(sa)^{-1} \sin sa} \frac{\epsilon^{pt}}{\cos sa}, \quad . \quad . \quad (246)$$

subject to the determinantal equation, over whose roots the summation extends, p being now algebraic. Effecting the differentiation indicated, we obtain

$$\mathbf{E} = -\frac{2h\nu}{4\pi k_1 r} \sum_{s} \frac{\cos sr - (sr)^{-1} \sin sr}{\cos sa} \epsilon^{pt}. \qquad (247)$$

The corresponding solution for the radial component of the magnetic force, say  $H_r$ , is

$$H_r = \left(\frac{2}{3}h\cos\theta\right) - 4h\cos\theta \sum_{s=0}^{\infty} \frac{\cos sr - (sr)^{-1}\sin sr}{s^2r^2\cos sa} \epsilon^{pt}. \quad (248)$$

At the centre of the sphere, let  $H_0$  be the intensity of the actual magnetic force. It is, by (248),

$$H_0 = \frac{2}{3}h\{1 + 2\sum (\cos sa)^{-1} \epsilon^{pt}\}.$$
 (249)

Thus the magnetic force arrives at the centre of the sphere in identically the same manner as current arrives at the distant end of an Atlantic cable according to the electrostatic theory, when a steady impressed force is applied at the beginning, with terminal short-circuits. In the case of the cable the first time-constant is

$$-p^{-1} = RSl^2/\pi^2$$
,

where Rl is the total resistance and Sl the total permittance. It is not greatly different from 1 second, so that, by (245), the sphere should be about a foot in radius to imitate, at its centre, the arrival curve of the cable.

To be precise we should not speak of magnetizing the sphere, because (ignoring the minute diamagnetism) it does not become magnetized. The principle, however, is the same. We set up the flux magnetic induction. But the magnetic terminology is defective. Perhaps it would be not objected to if we say we inductize\* the sphere, whether we magnetize it or not. This is, at any rate, better than extending the meaning of the word magnetize, which is already precise in the mathematical theory, though of uncertain application in practice, from the variable behaviour of iron.

<sup>\*</sup> Accent the first syllable, like magnetize. Practical men sometimes speak of energizing a core, &c. But energize is too general; by using inductize we specify what flux is set up.

40. The following is the alternative form of solution showing the waves, when  $c_1$  is finite. With the same assumption as before that  $v = \infty$  outside the sphere, the equation of  $\mathbf{H}_r$  the radial component of  $\mathbf{H}$  is

$$H_r = \frac{2\cos\theta}{q^2r^2} \frac{\cosh qr - (qr)^{-1}\sinh qr}{(qa)^{-1}\sinh qa}h, \quad . \quad . \quad (250)$$

which, at r=0, becomes

$$H_0 = \frac{2}{3} qa (\sinh qa)^{-1}h.$$
 . . . (251)

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Expand the circular function, giving

$$H_0 = \frac{4}{3} qa \epsilon^{-qa} (1 + \epsilon^{-2qa} + \epsilon^{-4qa} + \ldots) h$$
; (252)

or, since here  $q = v^{-1} \{ (p + \sigma)^2 - \sigma^2 \}^{\frac{1}{2}}$ ,

$$\mathbf{H}_{0} = \frac{4}{3} \frac{a}{v} e^{-\sigma t} (p + \sigma) \left( \frac{p - \sigma}{p + \sigma} \right)^{\frac{1}{2}} \left[ e^{-\frac{a}{v} (p^{2} - \sigma^{2})^{\frac{1}{2}}} + e^{-\frac{3a}{v} (p^{2} - \sigma^{2})^{\frac{1}{2}}} + \dots \right] (h e^{\sigma t}), \quad (253)$$

so, using (221), we get finally

$$\mathbf{H}_{0} = \frac{4}{3} h \frac{a}{v} e^{-\sigma t} (p+\sigma) \left[ \mathbf{J}_{0} \left\{ \frac{\sigma}{v} (a^{2} - v^{2} t^{2})^{\frac{1}{2}} \right\} + \mathbf{J}_{0} \left\{ \frac{\sigma}{v} (9a^{2} - v^{2} t^{2})^{\frac{1}{2}} \right\} + \dots \right]. (254)$$

The  $J_0$  functions commence when vt=a, 3a, 5a, &c., in succession, and the successive terms express the arrival of the first wave and of the reflexions from the surface which follow. In the case of pure diffusion, this reduces to

$$\mathbf{H}_{0} = (\frac{2}{3}h)2a(4\pi k_{1}\mu_{1}/\pi t)^{\frac{1}{2}} \left[ e^{-\pi k_{1}\mu_{1}a^{2}/t} + e^{-9\pi\mu_{1}k_{1}a^{2}/4t} + \ldots \right], \quad (255)$$

which is the alternative form of (249), involving instantaneous action at a distance. The theorem (in diffusion)

$$e^{-xp^{\frac{1}{2}}} \cdot p^{\frac{1}{2}}(1) = (\pi t)^{-\frac{1}{2}} e^{-x^2/4t}$$
 . . (256)

becomes generalized to

if

$$\epsilon^{-xq}q(1) = v^{-1}\epsilon^{-\sigma t}(p+\sigma) J_0\{\sigma v^{-1}(x^2 - v^2 t^2)^{\frac{1}{2}}\}, \quad (257)$$

$$q = v^{-1}(p^2 + 2\sigma p)^{\frac{1}{2}}.$$

On the right side of (257), the p means, as usual, differentiation to t. The two quantities  $\sigma$  and v may have any positive values; to reduce to (256) make v infinite whilst keeping  $\sigma/v^2$  finite.

41. Diffusion of Waves from a centre of impressed force in a conducting medium.—In equation (206) let a be infinitely

small. It then becomes

$$H = \frac{1}{3}a^3vr^{-2}(4\pi k + cp)(1 + qr)e^{-qr}f$$
, . (258)

the equation of H at distance r from an element of impressed *Phil. Mag.* S. 5. Vol. 26. No. 161. *Oct.* 1888. 2 B

electric force at the origin. Comparing with (233) we see that the solution of (258) may be derived, when f is constant, starting when t=0. Take g=0, making  $\rho=\sigma=4\pi k/2c$ . Then

$$H = \frac{H_0}{4\pi k} (4\pi k + cp) \left\{ e^{-\sigma t} \frac{r}{v} (p + \sigma) J_0 \left[ \frac{\sigma}{v} (r^2 - v^2 t^2)^{\frac{1}{2}} \right] + X_r \right\}, (259)$$

where  $X_r$  is what the  $X_a$  of (237) becomes on changing a to r; and

 $H_0 = \nu k r^{-2} \times \text{vol. integral of } f$ , . . . (260)

supposing the impressed force to be confined to the infinitely small sphere, so that its volume-integral is the "electric moment," by analogy with magnetism. The solution (259) begins at r as soon as t=r/v. It is true from infinitely near the origin to infinitely near the front; but no account is given of the state of things at the front itself.  $H_0$  is the final value of H. We may also write  $X_r$  thus,

$$\epsilon^{\sigma t} \mathbf{X}_{r} = 1 + \int_{r}^{vt} \frac{dr}{v} (\sigma + p) \mathbf{J}_{0} \left\{ \frac{\sigma}{v} (r^{2} - v^{2} t^{2})^{\frac{1}{2}} \right\} ;$$
 (261)

and (259) may also be written

$$\mathbf{H} = \frac{\mathbf{H}_0}{4\pi k} (4\pi k + cp) \left(1 - r\frac{d}{dr}\right) \mathbf{X}_r. \quad . \quad (262)$$

When c=0, (259) or (262) reduce to

$$\mathbf{H} = \mathbf{H}_{0} \left[ \left( \frac{2}{\pi} \right)^{\frac{1}{2}} y e^{-\frac{1}{2}y^{2}} + 1 - \left( \frac{2}{\pi} \right)^{\frac{1}{2}} \left\{ y - \frac{1}{|\underline{3}|} y^{3} + \frac{1 \cdot 3}{|\underline{5}|} y^{5} - \dots \right\} \right], (263)$$

where  $y = (2\pi\mu k r^2/t)^{\frac{1}{2}}$ .

42. Conducting sphere in nonconducting dielectric. Circular vorticity of e. Complex reflexion. Special very simple case.—At distance r from the origin, outside the sphere of radius a, which is the seat of vorticity of e, represented by  $f\nu$ , we have

$$H = \phi^{-1}(W/W_a) f va/r.$$
 . . (264)

The operator  $\phi$  will vary according to the nature of things on both sides of r=a. When it is a uniform conducting medium inside, and nonconducting outside, to infinity, we shall have

$$\phi = \phi_1 + \phi_2,$$

where  $\phi_1$ , depending upon the inner medium, is given by

$$\phi_1 = \frac{q_1}{4\pi k_1 + c_1 p} \frac{\{1 + (q_1 a)^{-2}\}\sinh q_1 a - (q_1 a)^{-1}\cosh q_1 a}{\cosh q_1 a - (q_1 a)^{-1}\sinh q_1 a}, (265)$$

and  $\phi_2$ , depending upon the outer medium, is given by

$$\phi_2 = \mu v \frac{1 + (qa)^{-1} + (qa)^{-2}}{1 + (qa)^{-1}}.$$
 (266)

The solution arising from the sudden starting of f constant is therefore

$$\mathbf{H} = (f \nu a/r) \Sigma (\mathbf{W}/\mathbf{W}_a) (p \cdot d\phi/dp)^{-1} \epsilon^{pt}, \qquad (267)$$

where p is now algebraical, and the summation ranges over the roots of  $\phi=0$ . There is no final H in this case, if we assume g=0 all over. But the determinantal equation is very complex, so that this (267) solution is not capable of easy interpretation. The wave method is also impracticable, for a similar reason.

In accordance, however, with Maxwell's theory of the impermeability of a "perfect" conductor to magnetic induction from external causes, the assumption  $k_1 = \infty$  makes the solution depend only upon the dielectric, modified by the action of the boundary, and an extraordinary simplification results.  $\phi_1$  vanishes, and the determinantal equation becomes  $\phi_2 = 0$ , which has just two roots,

$$qa = pa/v = -\frac{1}{2} + i\left(\frac{3}{4}\right)^{\frac{1}{2}};$$
 . . . (268)

and these, used in (267), give us the solution

$$H = (f v a/3 \mu v r) e^{-z} \{3 \cos -3^{\frac{1}{2}} (1 - 2a/r) \sin \} z \sqrt{3}, \quad (269)$$
where  $z = \{vt - (r - a)\}/2a$ .

Correspondingly, the tangential and radial components of E are

$$\mathbf{E} = \mu v \mathbf{H} + f v a^3 r^{-3} \left[ 1 - \frac{1}{3} \epsilon^{-z} (3 \cos + 3^{\frac{1}{2}} \sin) z \sqrt{3} \right] \quad . \tag{270}$$

$$\mathbf{F} = \frac{2a^3}{r^3} f \cos \theta \left[ 1 - \frac{1}{3} \frac{r}{a} e^{-z} \left( \frac{3a}{r} \cos - \sqrt{3} \left( 2 - \frac{a}{r} \right) \sin \right) z \sqrt{3} \right]. \quad (271)$$

This remarkably simple solution, considering that there is reflexion, corroborates Prof. J. J. Thomson's investigation\* of the oscillatory discharge of an infinitely conducting spherical shell initially charged to surface-density proportional to the sine of the latitude, for, of course, it does not matter how thin or thick the shell may be when infinitely conducting, so that it may be a solid sphere. (269) to (271) show the establishment of the permanent state. Take off the impressed force,

<sup>\* &</sup>quot;On Electrical Oscillations and the Effects produced by the Motion of an Electrified Sphere," Proc. Math. Soc. vol. xv. p. 210.

and the oscillatory discharge follows. But the impressed force keeping up the charge on the sphere need not be an external cause, as supposed in the paper referred to. There seems no other way of doing it than by having impressed force with vorticity  $f\nu$  on the surface, but in other respects it is immaterial whether it is internal or external, or superficial.

It may perhaps be questioned whether the sphere does reflect, seeing that its surface is the seat of f. But we have only to shift the seat of f to an outer spherical surface in the dielectric, to see at once that the surface of the conductor is the place of continuous reflexion of the wave incident upon it coming from the surface of f. The reflexion is not, however, of the same simple character that occurs when a plane wave strikes a plane boundary ( $k=\infty$ ) flush, which consists merely in sending back again every element of  $\mathbf{H}$  unchanged, but with its  $\mathbf{E}$  reversed; the curvature makes it much more complex. When we bring the surface of f right up to the conducting sphere, we make the reflexion instantaneous. At the front of the wave we have z=0 and

$$H = fva/\mu vr = E/\mu v$$

by (269) and (270). This is exactly double what it would be were the conductor replaced by dielectric of the same kind as outside, the doubling being due to the instantaneous reflexion of the inward going wave by the conductor.

The other method of solution may also be applied, but is rather more difficult. We have

$$\mathbf{H} = \frac{a\nu}{\mu vr} e^{-q(r-a)} \left(1 + \frac{1}{qr}\right) \left(1 - \frac{1}{qa}\right) \left(1 - \frac{1}{q^3 a^3}\right)^{-1} f. \quad (272)$$

Expand the last factor in descending powers of  $(qa)^3$ , and integrate. The result may be written

$$H = \frac{afv}{\mu vr} \left( \frac{d^2}{dx^2} + {a \choose r} - 1 \right) \left( \frac{d}{dx} - \frac{a}{r} \right) \left( \frac{x^2}{|2|} + \frac{x^5}{|5|} + \frac{x^8}{|8|} + \dots \right), (273)$$

where  $x=a^{-1}(vt-r+a)$ . Conversion to circular functions reproduces (269).

42 A. Same case with finite Conductivity. Sinusoidal Solution.—It is to be expected that with finite conductivity, even with the greatest at command, or  $k=(1600)^{-1}$ , the solution will be considerably altered, being controlled by what now happens in the conducting sphere. To examine this point, consider only the value of H at the boundary. We have, by (264),

$$H_a = \phi^{-1} f \nu = (\phi_1 + \phi_2)^{-1} f \nu$$
. (274)

Let f vary sinusoidally with the time, and observe the behaviour of  $\phi_1$  and  $\phi_2$  as the frequency changes. The full development which I have worked out is very complex. But it is sufficient to consider the case in which k is big enough, in concert with the radius a and frequency  $n/2\pi$ , to make the disturbances in the sphere be practically confined to a spherical shell whose depth is a small part of the radius. Let  $s = (2\pi\mu_1k_1na^2)^{\frac{1}{2}}$ ; then our assumption requires  $e^{-s}$  to be small. This makes

$$\phi_1 = -\frac{1}{4\pi k_1 a} \left( 1 - 2s^2 \frac{s + i(s - 1)}{1 - 2s + 2s^2} \right), \quad (275)$$

and, if further, s itself be a large number, this reduces to

$$\phi_1 = (1+i) (\mu_1 n/8\pi k_1)^{\frac{1}{2}} \dots (276)$$

Adding on the other part of  $\phi$ , similarly transformed by  $p^2 = -n^2$ , we obtain

$$\phi = \left(\mu v \frac{(na/v)^2}{1 + (na/v)^2} + \left(\frac{\mu_1 n}{8\pi k_1}\right)^{\frac{1}{2}}\right) - i\left(\frac{\mu v}{(na/v) + (na/v)^3} - \left(\frac{\mu_1 n}{8\pi k_1}\right)^{\frac{1}{2}}\right), (277)$$

where the terms containing  $k_1$  show the difference made by its not being infinite. The real part is very materially affected. Thus, copper, let

$$k_1 = (1600)^{-1}$$
,  $\mu_1 = 1$ ,  $2\pi n = 1600$ ,  $\alpha = 10$ ,  $s = 10$ .

These make s large enough. Now na/v is very small, but, on the other hand,

$$(\mu_1 n/8\pi k_1)^{\frac{1}{2}} = 130,$$

so that the real part of  $\phi$  depends almost entirely on the sphere, whilst the other part is little affected.

Now make n extremely great, say na/v = 1; else the same.

Then

$$\phi = (\frac{3}{2} \times 10^{10} + 44 \times 10^4) - i(\frac{3}{2} \times 10^{10} - 44 \times 10^4),$$

from which we see that the dissipation in space has become relatively important. The ultimate form, at infinite frequency, is

$$\phi = \mu v + (\mu_1 n / 8\pi k_1)^{\frac{1}{2}} (1+i);$$
 (278)

so that we come to a third state, in which the conductor puts a stop to all disturbance. This is, however, because it has been assumed not to be a dielectric also, so that inertia ultimately controls matters. But if, as is infinitely more probable, it is a dielectric, the case is quite changed. We shall have

$$\phi_1 = (4\pi g_1 + \mu_1 \ p^{\frac{1}{2}} (4\pi k_1 + c_1 p)^{-\frac{1}{2}}, \quad . \quad . \quad (279)$$

when the frequency is great enough, and this tends to  $\mu_1 v_1$ ,  $\mu_1$  being the inductivity and  $v_1$  the speed in the conductor, whatever g and k may be, provided they are finite. Thus, finally,

 $\phi = \mu_1 v_1 + \mu v \quad . \quad . \quad . \quad . \quad (280)$ 

represents the impedance, or ratio of  $f\nu$  to  $H_a$ , which are now in the same phase.

At any distance outside we know the result by the dielectric solution for an outward wave. But there is only super-

ficial disturbance in the conducting sphere.

43. Resistance at the front of a wave sent along a wire.—In its entirety this question is one of considerable difficulty, for two reasons, if not three. First, although we may, for practical purposes, when we send a wave along a telegraphcircuit, regard it as a plane wave, in the dielectric, on account of the great length of even the short waves of telephony, and the great speed, causing the lateral distribution (out from the circuit) of the electric and magnetic fields to be, to a great distance, almost rigidly connected with the current in the wires and the charges upon them; yet this method of representation must to some extent fail at the very front of the wave. Secondly, we have the fact that the penetration of the electromagnetic field into the wires is not instantaneous; this becomes of importance at the front of the wave, even in the case of a thin wire, on account of the great speed with which it travels over the wire \*. The resistance per unit length must vary rapidly at the front, being much greater there than in the body of the wave; thus causing a throwing back, equivalent to electrostatic or "jar" retardation.

Now, according to the electromagnetic theory, the resistance must be infinitely great at the front. Thus, alternate the current sufficiently slowly, and the resistance is practically the steady resistance. Do it more rapidly, and produce appreciable departure from uniformity of distribution of current in the wire, and we increase the resistance to an amount calculable by a rather complex formula. But do it

<sup>\*</sup> The distance within which, reckoned from the front of the wave backward, there is material increased resistance, we may get a rough idea of by the distance travelled by the wave in the time reckoned to bring the current-density at the axis of the wire to, say, nine tenths of the final value. It has all sorts of values. It may be 1 or 1000 kilometres, according to the size of wire and material. At the front, on the assumption of constant resistance, the attenuation is according to  $e^{-Rt/2L}$ , R being the resistance, and L the inductance of the circuit per unit length. Hence the importance of the increased resistance in the present question.

very rapidly, and cause the current to be practically confined to near the boundary, and we have a simplified state of things in which the resistance varies inversely as the area of the boundary, which may, in fact, be regarded as plane. The resistance now increases as the square root of the frequency, and must therefore, as said, be infinitely great at the front of a wave, which is also clear from the fact that penetration is

only just commencing.

But for many reasons, some already mentioned, it is far more probable that the wire is a dielectric. If, as all physicists believe, the æther permeates all solids, it is certain that it is a dielectric. Now this becomes of importance in the very case now in question, though of scarcely any moment otherwise. Instead of running up infinitely, the resistance per unit area of surface of a wire tends to the finite value  $4\pi\mu_1v_1$ . This is great, but far from infinity, so that the attenuation and change of shape of wave at its front produced by the throwing back cannot be so great as might otherwise be expected.

Thus, in general, at such a great frequency that conduction is nearly superficial, we have, if  $\mu$ , c, k, and g belong to the

wire,

$$E/H = (4\pi g + \mu p)^{\frac{1}{2}} (4\pi k + cp)^{-\frac{1}{2}}, . . . (281)$$

if E is the tangential electric force and H the magnetic force, also tangential, at the boundary of a wire. Now let R' and L' be the resistance and inductance of the wire per unit of its length. We must divide H by  $4\pi$  to get the corresponding current in the wire, as ordinarily reckoned. So  $4\pi A^{-1}$  times the right number of (281) is the resistance-operator of unit length, if A is the surface per unit length; so, expanding (281), we get

R' or L'n=
$$\frac{4\pi}{\Lambda} \frac{\mu v}{\sqrt{2}} \left\{ \left( \frac{4\rho_2^2 + n^2}{4\rho_1^2 + n^2} \right)^{\frac{1}{2}} \pm \frac{4\rho_1\rho_2 + n^2}{4\rho_1^2 + n^2} \right\}^{\frac{1}{2}}$$
, (282)

where  $\rho_1$ ,  $\rho_2$  are as before, in (208). Here  $n/2\pi =$  frequency. Disregarding g, and  $\rho_2$ , we have

R' or 
$$L'n = (\frac{1}{2})^{\frac{1}{2}} 4\pi \mu v A^{-1} \{B \pm B^2\}^{\frac{1}{2}}, . (283)$$

where

$$B = n(4\rho_1^2 + n^2)^{-\frac{1}{2}} = nc\{(4\pi k)^2 + n^2c^2\}^{-\frac{1}{2}}.$$

When c is zero, R' and L'n tend to equality, as shown by Lord Rayleigh. But when c is finite, L'n tends to zero, and R' to  $4\pi\mu\nu\Lambda^{-1}$ , as indeed we can see from (281) at once, by the relative evanescence of k and g, when finite.

But the frequency needed to bring about an approximation towards the constant resistance is excessive; in copper, we require trillions per second. This brings us to the third reason mentioned; we have no knowledge of the properties of matter under such circumstances, or of æther either. The net result is that although it is infinitely more probable that the resistance should tend to constancy than to infinity, yet the real value is quite speculative\*. Similar remarks apply to sudden discharges, as of lightning along a conductor. The above R', it should be remarked, is real resistance, in spite of its ultimate form, suggestive of impedance without resistance †. The present results are corroborative of those in Part I., and, in fact, only amount to a special application of the same.

44. Reflecting Barriers.—Let the medium be homogeneous between  $r=a_0$  and  $r=a_1$ , where there is a change of some kind, yet unstated. Let between them the surface r=a be a sheet of vorticity of e of the first order. We already know what will happen when  $f\nu$  is started, for a certain time, until in fact the inward wave reaches the inner boundary, and, on the other side, until the outward wave reaches the outer boundary; though, unless the surface of f is midway between the boundaries, the reflected wave from the nearest barrier will reach into a portion of the region beyond f, by the time the further barrier is reached by the primary wave. The

† There is a tendency at present amongst some writers to greatly extend the meaning of resistance in electromagnetism; to make it signify cause/effect. This seems a pity, owing to the meaning of resistance having been thoroughly specialized in electromagnetism already, in strict relationship to "frictional" dissipation of energy. What the popular meaning of "resistance" may be is beside the point. I would suggest that what is now called the magnetic resistance be called the magnetic reluctance; and per unit volume, the reluctancy.

<sup>\*</sup> The above was written before the publication of Professor Lodge's highly interesting lectures before the Society of Arts. Some of the experiments described in his second lecture are seemingly quite at variance with the electromagnetic theory. I refer to the smaller impedance of a short circuit of fine iron wire than of thick copper, as reckoned by the potential-difference at its beginning needed to spark across the circuit between knobs. Should this be thoroughly verified, it has occurred to me as a possible explanation that things may be sometimes so nicely balanced that the occurrence of a discharge may be determined by the state of the skin of the wire. A wire cannot be homogeneous right up to its boundary, with then a perfectly abrupt transition to air; and the electrical properties of the transition-layer are unknown. In particular, the skin of an iron wire may be nearly unmagnetizable,  $\mu$  varying from 1 to its full value, in the transition-layer. Consequently, in the above formula, resistance  $4\pi\mu\nu$ per unit surface, we may have to take  $\mu=1$  in the extreme, in the case of an iron wire. But even then, the explanation of Professor Lodge's results is capable of considerable elucidation. Perhaps resonance will do it.

subsequent history depends upon the constitution of the media beyond the boundaries, which can be summarized in two boundary conditions. The expression for E/H is, in general,

$$\frac{E}{H} = -(4\pi k + cp)^{-1} \frac{u' - yw'}{u - yw'}, \quad . \quad . \quad (284)$$

by (120), extended, the extension being the introduction of y, which is a differential operator of unstated form, depending upon the boundary conditions. Let  $y_0$  and  $y_1$  be the y's on the inner and outer side of the surface of f. The differential equations of  $H_a$ , the magnetic force there, is then

$$f_{\nu} = \{ (E/H)_{(out)} - (E/H)_{(in)} \} H_a, \quad . \quad (285)$$

as in § 19. Applying (284) and the conjugate property (114) of the functions u and w, (since there is no change of medium at the surface of f), this becomes

$$H_a = \frac{4\pi k + cp}{q} \frac{(u_a - y_0 w_a)(u_a - y_1 w_a)}{y_1 - y_0} f\nu; \quad . \quad (286)$$

from which the differential equation of H at any point between  $a_0$  and a is obtained by changing  $u_a-y_0w_a$  to  $(a/r)(u-y_0w)$ ; and at any point between a and  $a_1$  by changing  $u_a-y_1w_a$  to  $(a/r)(u-y_1w)$ .

Unless, therefore, there are singularities causing failure,

the determinantal equation is

$$y_1 - y_0 = 0, \dots (287)$$

and the complete solution between  $a_0$  and  $a_1$  due to f constant may be written down at once. Thus at a point outside the surface of f we have

(out) 
$$H = \frac{4\pi k + cp}{q} \frac{a}{r} \frac{(u_a - y_0 w_a)(u - y_1 w)}{y_1 - y_0} f v = \phi^{-1} f;$$
 (288)

and therefore, if f starts when t=0,

$$\mathbf{H} = \frac{f}{\phi_0} + \frac{fa\nu}{r} \sum \frac{(u_a - yw_a)(u - yw)}{p(d/dp)(y_1 - y_0)} \cdot \frac{4\pi k + cp}{q} \, \epsilon^{pt}, \quad (289)$$

p being now algebraic, given by (287);  $\phi_0$  the steady  $\phi$ , from (218); and y the common value of the (now) equal y's; which identity makes (289) applicable on both sides of the surface of f.

45. Construction of  $y_1$  and  $y_0$ .—In order that  $y_1$  and  $y_0$  should be determinable in such a way as to render (286) true, the media beyond the boundaries must be made up of any

number of concentric shells, each being homogeneous, and having special values of c, k,  $\mu$ , and g. For the spherical functions would not be suitable otherwise, except during the passage of the primary waves to the boundaries, or until they reached places where the departure from the assumed constitution commenced. Assuming the constitution in homogeneous spherical layers, there is no difficulty in building up the forms of  $y_0$  and  $y_1$  in a very simple and systematic manner, wholly free from obscurities and redundancies. In any layer the form of E/H is as in (284), containing one y. at the boundary of two layers E is continuous, and also H (provided the physical constants are not infinite), so E/H is continuous. Equating, therefore, the expressions for E/H in two contiguous media expresses the y of one in terms of the y of the other. Carrying out this process from the origin up to the medium between  $a_0$  and  $a_1$  expresses  $y_0$  in terms of the y of the medium containing the origin; this is zero, so that  $y_0$  is found as an explicit function of the values of u, w, u', w' at all the boundaries between the origin and  $a_0$ . In a similar manner, since the y of the outermost region, extending to infinity, is 1, we express  $y_1$ , belonging to the region between a and  $a_1$ , in terms of the values of u, &c. at all the boundaries between a and  $\infty$ . Each of these four functions will occur twice for each boundary, having different values of the physical constants with the same value of r. I mention this method of equation of E/H operators because it is a far simpler process than what we are led to if we use the vector and scalar potentials; for then the force of the flux has three component vectors—the impressed force, the slope of the scalar potential, and the time-rate of decrease of the vector potential. The work is then so complex that a most accomplished mathematician may easily go wrong over the boundary conditions. These remarks are not confined in application to spherical waves.

If an infinite value be given to a physical constant, special forms of boundary condition arise, usually greatly simplified; e.g. infinite conductivity in one of the layers prevents electromagnetic disturbances from penetrating into it from without;

so that they are reflected without loss of energy.

Knowing  $y_1$  and  $y_0$  in (288), we virtually possess the sinusoidal solution for forced vibrations, though the initial effects, which may or may not subside or be dissipated, will require further investigation for their determination; also the solution in the form of an infinite series showing the effect of suddenly starting f constant; also the solution arising from any initial distribution of  $\mathbf{E}$  and  $\mathbf{H}$  of the kind appro-

priate to the functions, viz. such as may be produced by vorticity of e in spherical layers, proportional to  $\nu$  (or  $\nu Q_m$  in general). But it is scarcely necessary to say that these solutions in infinite series, of so very general a character, are more ornamental than useful. On the other hand, the immediate integration of the differential equations to show the development of waves becomes excessively difficult, from the great complexity, when there is a change of medium to produce reflexion.

46. Thin Metal Screens.—This case is sufficiently simple to be useful. Let there be at  $r=a_1$  a thin metal sheet interposed between the inner and outer nonconducting dielectrics, the latter extending to infinity. If made infinitely thin, E is continuous, and H discontinuous to an amount equal to  $4\pi$  times the conduction current (tangential) in the sheet. Let  $K_1$  be the conductance of the sheet (tangential) per unit area; then

$$(H/E)_{in} - (H/E)_{out} = 4\pi K_1$$
 at  $r = a_1$ .

Therefore by (284), when the dielectric is the same on both sides,

$$cp\left(\!\frac{u_1\!-\!w_1}{u_1'\!-\!w_1'}\!-\!\frac{u_1\!-\!y_1w_1}{u_1'\!-\!y_1w_1'}\!\right)\!=\!4\pi\mathbf{K}_1,$$

where the functions  $u_1$ , &c. have the  $r=a_1$  values. From this,

$$y_{1} = \frac{1 - (4\pi K_{1}/cpq)u_{1}'(u_{1}' - w_{1}')}{1 - (4\pi K_{1}/cpq)w_{1}'(u_{1}' - w_{1}')} . . . (290)$$

expresses  $y_1$  for an outer thin conducting metal screen, to be used in (286). If of no conductivity, it has no effect at all, passing disturbances freely, and  $y_1=1$ . At the other extreme we have infinite conductivity, making  $y_1=u_1'/w_1'$ , with complete stoppage of outward-going waves, and reflexion without absorption, destroying the tangential electric disturbance.

When the screen, on the other hand, is within the surface of f, say, at  $r=a_0$ , of conductance  $K_0$  per unit area, we shall find

$$y_0 = \frac{(4\pi K_0/cpq)u_0'^2}{1 + (4\pi K_0/cpq)u_0'w_0''}, \quad . \quad . \quad (291)$$

where  $u_0$ , &c. have the  $r=a_0$  values. The difference of form from  $y_1$  arises from the different nature of the r functions in the region including the origin. As before, no conductivity gives transparency  $(y_0=0)$ , and infinite conductivity total reflexion  $(y_0=u_0'/w_0')$ . When the inner screen is shifted up to the origin, we make  $y_0=0$  and so remove it.

47. Solution with outer screen;  $K_1 = \infty$ ; f constant.—Let there be no inner screen and let the outer be perfectly conducting. As J. J. Thomson has considered these screens\*, I will be very brief, regarding them here only in relation to the sheet of f and to former solutions. The determinantal equation is

$$u_1' = 0$$
, or  $\tan x = x(1-x^2)^{-1}$ , . . . (292)

if x=ipa/v. Roots nearly  $\pi$ ,  $2\pi$ ,  $3\pi$ , &c.; except the first, which is considerably less. The solution due to starting f constant, by (289) is therefore

$$\mathbf{H} = (f v a / \mu v r) \Sigma (u u_a w_1' / a_1 u_1'') \epsilon^{pt}; \qquad (293)$$

which, developed by pairing terms, leads to

$$H = \frac{fva}{\mu vr} \sum_{x=0}^{x^{4} - x^{2} + 1} 2 \sin \frac{vtx}{a_{1}} \left(\cos - \frac{a_{1}}{xr} \sin \frac{vtx}{a_{1}} \left(\cos - \frac{a_{1}}{xa} \sin \frac{vtx}{a_{1}} \right) - \frac{vtx}{a_{1}} \left(\cos - \frac{vtx}{a_{1}} \right) - \frac{vtx}{a_{1}} \left(\cos -$$

which of course includes the effects of the infinite series of reflexions at the barrier. By making  $a_1 = \infty$ , however, the result should be the same as if the screen were non-existent, because an infinite time must elapse before the first reflexion can begin, and we are concerned only with finite intervals. The result is

$$H = \frac{fva}{\mu vr} \cdot \frac{2}{\pi} \int_{0}^{\infty} dx_{1} \frac{\sin x_{1}vt}{x_{1}} \left(\cos - \frac{1}{x_{1}r}\sin\right) x_{1}r \left(\cos - \frac{1}{x_{1}a}\sin\right) x_{1}a, \quad (295)$$

which must be the equivalent of the simple solution (142) of § 21, showing the origin and progress of the wave.

Now reduce it to a plane wave. We must make a infinite, and r-a=z finite. Also take fv=e, constant. We then have

$$H = \frac{e}{4\mu v} \frac{2}{\pi} \int_0^\infty dx_1 \left( \sin \frac{x_1(vt-z)}{x_1} + \frac{\sin x_1(vt+z)}{x_1} \right), \quad (296)$$

showing the H at x due to a plane sheet of vorticity of e situated at z=0. This is the equivalent of the solution (12) of § 2, indicating the continuous uniform emission of  $H=e/2\mu v$  both ways from the plane z=0.

Returning to (294), it is clear that from t=0 to  $t=(a_1-a)/v$ , the solution is the same as if there were no screen. Also if a is a very small fraction of  $a_1$ , the electromagnetic wave of depth 2a will, when it strikes the screen, be reflected nearly as from a plane boundary. It would therefore seem that this

<sup>\*</sup> In the paper before referred to.

wave would run to and from between the origin and boundary unceasingly. This is to a great extent true; and therefore there is no truly permanent state (the electric flux, namely, alone); but examination shows that the reflexion is not clean, on account of the electrification of the boundary, so that there is a spreading of the magnetic field all over the region within the screen.

48. Alternating f with reflecting barriers. Forced vibrations.—Let the medium be nonconducting between the boundaries  $a_0$  and  $a_1$ . Equation (288) then becomes

$$H = \frac{va}{\mu vr} \frac{(u_a - y_0 w_a)(u - y_1 w)}{y_1 - y_0} f, \quad . \quad . \quad (297)$$

giving H outside the surface of f. We see that  $y_0=0$  and  $u_a=0$  make H=0. That is, the forced vibrations are confined to the inside of the surface of f only, at the frequencies given by  $u_a=0$ , provided there is no internal screen to disturb, but independently of the structure of the external medium (since  $y_1$  is undetermined so far), with possible exceptions due to the vanishing of  $y_1$  simultaneously. But (297), sinusoidally realized by  $p^2=-n^2$ , does not represent the full final solution, unless the nature of  $y_0$  and  $y_1$  is such as to allow the initial departure from this solution to be dissipated in space or killed by resistance. Ignoring the free vibrations, let  $y_0=0$ , and  $y_1=u_1'/w_1'$ , meaning no internal, and an infinitely conducting external screen. Then

(out) 
$$H = (va/\mu vr)u_a \{uw_1'/u_1' - w\}f$$
,  
(in)  $H = (va/\mu vr)u \{u_aw_1'/u_1' - w_a\}f$ . (298)

If  $w_1'=0$ , or in full,

$$(v/na_1)\tan(na_1/v)=1-(v/na_1)^2$$
,

we obtain a simplification, viz.

$$\mathbf{H}_{(\text{in or out})} = -(\nu a/\mu vr)(uw_u \text{ or } u_a w)f; \quad . \quad . \quad (299)$$

and the corresponding tangential components of electric force are

$$E_{\text{(in or out)}} = (va/\mu vr)(u'w_a \text{ or } u_a w')(cp)^{-1}f.$$
 (300)

But if  $u_1'=0$ , the result is infinite. This condition indicates that the frequency coincides with that of one of the free vibrations possible within the sphere  $r=a_1$  without impressed force. But, considering that we may confine our impressed force to as small a space as we please round the origin, the

infinite result is not easily understood, as regards its deve-

lopment.

But the development of infinitely great magnetic force by a plane sheet of f is very easily followed in full detail, not merely with sinusoidal f, but with f constant. Considering the latter case, the emission of H is continuous, as before described, from the surface of f. Now place a plane infinitely conducting barrier parallel to f, say on the left side. We at once stop the disturbances going to the left and send them back again, unchanged as regards H, reversed as regards E. The **H** disturbance on the left side of f therefore commences to be doubled after the time a/v has elapsed, a being the distance of the reflecting barrier from the plane of f, and on the right side after the interval 2a/v. Next, put a second infinitely conducting barrier on the right side of f. It also doubles the H disturbances as they arrive; so that, by the inclusion of the plane of f between impermeable barriers, combined with the continuous emission of H, the magnetic disturbance mounts up infinitely, in a manner which may be graphically followed with ease. Similarly, with f alternating, at particular frequencies depending upon the distances of the two barriers from f.

Returning to the spherical case, an infinitely conducting

internal screen, with no external, produces

$$H_a = \frac{(u_a w_0' - w_a u_0') (u_a - w_a)}{\mu v(w_0' - u_0')} f \nu. \qquad (301)$$

We cannot produce infinite H in this case, because the absence of an external barrier will not let it accumulate. Shifting the surface of f right up to the screen, or vice versa, simplifies matters greatly, reducing to the case of § 42.

May 8th, 1888.

XL. On Flux and Reflux of Water in Open Channels or in Pipes or other Ducts. By Professor James Thomson, LL.D., F.R.S.\*

IN the autumn of 1872 I was staying at a place named Castlerock, on the north coast of Ireland, between the mouth of the Bann River and the entrance to Lough Foyle.

<sup>\*</sup> Communicated by the Author, having been read in the British Association Meeting at Bath, 1888, Section A.

There was an extensive sandy beach there, lashed by the great waves of the Atlantic Ocean. At a part of that beach a small river or stream flowed to the sea; but the sandy beach had been thrown up as a bank, at about high-tide level, obstructing what might have been the direct outfall course for the stream into the sea, and causing the stream to turn to its right and to flow eastward for some distance along the back of that sandy bank before finding an opening for flow out to the sea. Thus, at the back of the bank, a little estuary was formed, along which, when the tide was down, the stream would have for a considerable length a nearly level bed; and into which, when the tide was up, the sea-water entered so as to fill it up to various depths according to the height of the sea-surface.

I happened to be watching with interest the motions of the water in the little estuary at a time when a considerable depth of water (such as a few feet depth along its mid-channel) was maintained in it by the height of the sea-water outside, and when the slow rising and sinking of the ocean-waves was producing in the estuary a flux and reflux on a small scale like that of the tidal flow in large estuaries\*. The motions of the water being indicated by numerous little pieces of seaweed carried in suspension, I noticed that the water at or very close to the channel-bed reversed its landward or seaward flow always much earlier than did the main body of the water in the channel, less affected by contiguity to the bed. The phenomenon being noticed, the reason at once became apparent. The lamina contiguous to the bed, or channel-face, would be always hindered by the frictional resistance of that face from getting into so great a velocity, either seaward or landward, as that which would be attained to by the main body of the water. Then, when the water at the sea-end of the estuary was raised in level, by the arrival of an ocean-wave, so as to give a gravitational propulsive influence tending to cause the water to flow landward along the estuary, the main body of the water, in virtue of its inertia with seaward momentum, would continue to flow for some time seaward, flowing as it were uphillt; while the frictionally restrained lamina at the channel-face, being nearly devoid of inertial tendency seaward, would readily yield to the landward gravitational propulsive influ-

<sup>\*</sup> The period of these oscillations may be about from 10 to 20 seconds; as I have been informed that Prof. Stokes has found, by observations on that coast, that the period from one wave to the next, in the large Atlantic waves there, is at most about 17 seconds.

<sup>†</sup> Or, in more precise terms, flowing from a place of lower to a place of higher free-level.

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ence due to the landward surface declivity of the water in the

estuary.

Exactly a like explanation, mutatis mutandis, is applicable to the case of reversal of the flow from having been landward to its becoming seaward. The channel-face lamina makes its reversal of flow, just as in the other case, earlier than does the

main body of the water, and for like reason.

It may now further be noticed that precisely corresponding phenomena would present themselves in the flux and reflux of water in a pipe; if, for instance, the pipe were connecting two cisterns, and a plunger were kept oscillating upwards and downwards in one of them so as to cause the alternating flow through the pipe. The phenomena might be very interestingly manifested in an open trough connecting two cisterns, arrangements being made, by a plunger or otherwise, for causing flux and reflux along the trough, and the motions of the water being indicated by small visible particles in suspension in the water, or by the dropping in of granules of aniline

dye.

It may now be worthy of remark that the hydraulic principle brought into notice in the present paper, in respect to Flux and Reflux along Channels, is closely allied to, and is in some respects identical with, the leading principle set forth in previous papers by myself on the Flow of Water round Bends in Rivers, &c. In that case the frictionally resisted and retarded lamina in contiguity with the channel-face, or bed, flows transversely (or rather obliquely) across the channel towards the inner bank of the bend, impelled inwards by gravitational propulsive influence (that is, downhill as it were). while the main body of the stream, flowing quicker in the bend, exerts centrifugal force outwards, or tends inertially out towards the outer bank. The papers here referred to on Flow of Water round Bends in Rivers, &c. are to be found in the 'Proceedings of the Royal Society' for May 1876; in the British Association Report for the Glasgow Meeting, 1876, Section A, page 31 of Transactions of the Sections; in the 'Proceedings of the Royal Society,' 1877, No. 182, page 356; and in the 'Proceedings of the Institution of Mechanical Engineers,' August 1879, p. 456. Also some other important cases in which like principles of fluid motion come into play (in Whirlwinds &c.) are adduced in a paper by myself in the British Association Report for the Montreal Meeting, 1884, Section A, page 641.

The University, Glasgow, September 5, 1888.

### XLI. The Law of Dispersion. By Edward Wilson, M.A.\*

LORD RAYLEIGH, in his address to the British Association at Montreal, took occasion to observe that Professor S. P. Langley's demonstration of the inaccuracy of Cauchy's formula for the law of dispersion would have an

important bearing on optical theory.

An abstract of this important demonstration is to be found in the Philosophical Magazine, March 1884. It thus appears that the true form of the function  $\phi$  in the equation  $\mu = \phi(\lambda)$  remains to be discovered; and yet it is scarcely possible to overrate the importance of its determination, for without it not a single step can be taken in tracing a connexion between the chemical constitution of a substance and its refractive powers.

The author holds with a somewhat deep conviction the

following propositions:—

(1) That before the refractive and dispersive properties of a liquid or solid substance can be made use of to determine its chemical constitution or molecular structure, it is absolutely imperative to determine the form of the function  $\phi$  in the equation  $\mu = \phi(\lambda)$ .

(2) That it is the *constants* of this function which will have to be correlated with chemical constitution and molecular

structure.

The present paper is an attempt to supply the first of these desiderata; the second desideratum, though more difficult,

may possibly be attempted at a future time.

An incontestable form of  $\phi$  could only be furnished by a true Theory of Light, which it is to be feared is not likely to be obtained for some time to come. Meanwhile we must perforce be content to attempt the discovery of an empirical formula, the probability of which being true must chiefly depend upon the close agreement of its calculated results with those of observation.

Of such possible formulæ the following, which, as analogy would lead us to expect, assumes the exponential form, is

submitted for consideration.

If v be the velocity in a refracting substance of a ray of light of wave-length  $\lambda$ , and V the velocity in vacuo; then

$$\frac{v}{\nabla} = \left(a + b\lambda + \frac{c}{\lambda}\right)e^{-\frac{h}{\lambda^2}};$$

or, if V = unity, and  $\mu$  be the refractive index,

$$\frac{1}{\mu} = \left(a + b\lambda + \frac{c}{\lambda}\right)e^{-\frac{h}{\lambda^2}}.$$
 (1)

The wave-length of the ray, whose velocity in the refracting substance is the same as that in vacuo, is determined by the equation

$$a + b\lambda + \frac{c}{\lambda} = e^{\frac{h}{\lambda^2}}$$
  
= 1 very nearly. . . . . (2)

The ray of greatest wave-length which enters the refracting substance depends upon the angle of incidence; and, if this angle be  $\Theta$ , is determined by the equation

$$a + b\lambda + \frac{c}{\lambda} = \frac{e^{\frac{h}{\lambda^2}}}{\sin \Theta}$$
$$= \sqrt{2} \text{ very nearly} \qquad . \qquad . \qquad . \qquad (3)$$

if the angle of incidence = 45°.

All rays of wave-length intermediate between those determined by equations (2) and (3) travel faster in the refracting substance than they do in vacuo.

Professor Langley, in the following table \*, gives the wavelengths, with the probable errors, of the six ultra-red lines that he determines:—

Date of observation.	λ.	n.
April 1, 1882 April 9, ,, June 27, ,, June 13–27, ,, July 14, ,, June 7, ,,	$\mu \\ 1.010 \pm 0.0053 \\ 1.200 \pm 0.0069 \\ 1.658 \pm 0.0091 \\ 1.767 \pm 0.0094 \\ 2.090 \pm 0.0104 \\ 2.356 \pm 0.0110$	1·5654 1·5625 1·5562 1·5549 1·5511

But repeated investigations have shown that better results are obtained if three of these wave-lengths are altered within the limits of probable error.

For the Hilger prism used by Professor Langley in his investigation, the constants are

a = .6299284, b = .0058580, c = .0075571, b = .0071680.

With these constants the correspondence between observation and calculation is given in the following table:—

Ray.	$\mu$ . Observed.	$\mu$ . Calculated.	Difference.	
Н,	1.607000	1.606923	.000077	
F	1.589900	1.589955	.000055	
b <sub>4</sub>	1.586200	1.586233	.000033	
D <sub>1</sub>	1.579800	1.579800	.000000	
C	1.575700	1.575708	*000008	
A	1.571400	1.571392	.000008	
μ1.010	1.565400	1.565379	.000021	
$^{\mu}_{1.1931}$	1.562500	1.562450	.000050	
1.6671	1.556200	1.556256	.000056	
μ1.7764	1.554900	1.554905	.000005	
μ2·090	1.551100	1.551040	.000060	
μ2·356	1.547800	1.547742	000058	

If  $\lambda_{\mu=1}$  be the wave-length of the ray which travels as fast in the Hilger prism as *in vacuo*, and  $\lambda_G$  be the wave-length of the greatest ray which would enter the prism at an angle of incidence of 45°, then

$$\lambda_{\text{G}} = 63.5$$
 $\lambda_{\text{G}} = 133.8$ 

The only indices of refraction which have come to hand of sufficient accuracy to test a formula, are those of seven prisms determined by Dr. Hopkinson (Proc. R. S. June 14, 1877), and given by Professor Everett in 'Units and Physical Constants,' pp. 70 and 71, 1st edition; the results are as follows:—

Hard Crown Glass. Density 2:48575.

	$\mu$ .	μ.	
Ray.	Observed.	Calculated.	Difference
H,	1.532789	1.532789	.0000000
G	1.528348	1.528375	000027
F	1.523145	1.523147	$\cdot 000002$
E	1.520324	1.520329	.000005
D,	1.517116	1.517119	.000003
C'	1.514571	1.514576	$\cdot 000005$
В	1.513624	1.513642	.000018
A	1.511755	1.511761	.000006

#### Ray. Observed. Calculated. Difference. 1.531415 1.531415 H<sub>1</sub> ..... .000000 1.526592 1.526624.000032 1.5209941.520995.000001 1.518017 1.517988 .000029 1.514580 1.514589 .000009 1.511910 1.511913 .000003 1.510918 1.510932.000014 1.508956 1.508955 $\cdot 000001$

### Extra Light Flint Glass. Density 2.86636.

Ray.	$\mu$ . Observed.	$\mu$ . Calculated.	Difference.
H <sub>1</sub> G. F. E. D <sub>1</sub> C. B	1·562760	1·562760	*000000
	1·556375	1·556438	*000063
	1·549125	1·549125	*000000
	1·545295	1·545280	*000015
	1·541022	1·540998	*000024
	1·537682	1·537682	*000000
	1·536450	1·536477	*000027
	1·534067	1·534067	*000000

### Light Flint Glass. Density 3.20609.

Ray.	$\mu$ . Observed.	$\mu$ . Calculated.	Difference.
H <sub>1</sub> G. F. E D <sub>1</sub> B	1.600717	1.600717	*000000
	1.592825	1.592874	*000049
	1.583881	1.583881	*000000
	1.579227	1.579195	*000032
	1.574013	1.574014	*000001
	1.570007	1.570013	*000006
	1.568558	1.568558	*000000

### Dense Flint Glass. Density 3.65865.

Ray.	$\mu$ . Observed.	$\mu$ . Calculated.	Difference.
$egin{array}{c} \mathbf{H_1} & \dots & \\ \mathbf{G} & \dots & \\ \mathbf{F} & \dots & \\ \mathbf{E} & \dots & \end{array}$	1.656229 1.646071 1.634748 1.628882	1·656229 1·646168 1·634748 1·628858	*000000 *000097 *000000 *000024
$egin{array}{c} D_1 & \dots & \\ C & \dots & \\ B & \dots & \end{array}$	1.62532 1.622411 1.617477 1.615704	1.622411 1.617473 1.615700	·000000 ·000004 ·000004

Extra Dense Flint Glass. Density 3.88947.

Ray.	μ. Observed.	μ. Calculated.	Difference.
H <sub>1</sub> G F D <sub>1</sub> C B	1·688590 1·677020 1·664246 1·657631 1·650374 1·644871 1·642894 1·639143	1·688581 1·677186 1·664237 1·657571 1·650319 1·644865 1·642927 1·639135	*000009 *000166 *000009 *000060 *000055 *000006 *000033 *000008

### Double Extra Dense Flint Glass. Density 4:42162.

Ray.	$\mu$ . Observed.	$\mu.$ Calculated.	Difference.
G F E O B	1·743210 1·727257 1·719081 1·710224 1·703485 1·701080 1·696531	1·743210 1·727280 1·719080 1·710166 1·703485 1·701144 1·696530	·000000 ·000023 ·000001 ·000058 ·000000 ·000064 ·000001

Such is all the evidence that can at present be offered on behalf of the formula, but if further corroborative evidence should be forthcoming, and the *constants* properly correlated, chemists would find placed in their hands an instrument of prodigious power for the purpose of exploring the molecular constitution of bodies.

If any should think it presumptuous to attempt to succeed, where such eminent mathematicians as Cauchy, Redtenbacher, and Briot have failed, it ought to be borne in mind that, before the admirable researches of Professor Langley, success was almost impossible.

### XLII. Notices respecting New Books.

Geology: Chemical, Physical, and Stratigraphical. By Joseph Prestwich, M.A., F.R.S., F.G.S., &c. Vol. I. 1886; 477 pages, 6 maps and plates, 218 woodcuts. Vol. II. 1888; 606 pages, 2 maps, 18 plates of fossils, 256 woodcuts. 8vo. Clarendon Press, Oxford.

THE object and character of this work may be regarded as, first, aiming at a widely philosophical and yet minutely scientific exposition of the action of natural laws in Chemistry, Physics, and Biology, on and within the Earth; and, second, presenting especially

points of general interest, such as every intelligent reader, not being a geologist, may comprehend. For the most part the Chapters may be read as complete Essays on the many subjects necessary for a geological student to know, written in a fairly popular style, though enriched with all the necessary details and references to authorities.

In the First Volume the natural causes and methods of the wearing-away and decomposition of rock-masses, and the variable rearrangement of the resultant material are first of all explained. being highly important in the consideration of Denudation and its results—as to local decrease of land and accumulation of various deposits in water all over the globe. The water-question is specially treated by one who has traced the rain-water in its underground ways to natural springs and rivers, and to the supply of artificial wells and borings. The part played by water in volcanic eruptions. nearly a new subject, is fully described. Ice and snow have their special chapter also. Alterations in level of the earth's surface, whether effected by earthquakes, by the lateral pressure of great contractions, or by coral-growths, have their interesting and instructive chapters; and the important subjects of faults in disturbed strata, joints, cleavage, mineral veins, old volcanic rocks, metamorphism, and all the conditions of mountain-ranges, whether continental or local, are treated of in essays full of facts and bold generalizations. Chapters xviii. and xix., on metalliferous deposits. treat of their endless varieties of veins and lodes, their geological and geographical distribution, and the various results of their decompositions. All this is in close association with the foregoing subjects, and together with the preceding essays, while supplying the general reader with useful résumés of what is known, elucidated by many new ideas, meets the requirements of the advanced student. It enables him to understand more fully the various physical and chemical problems offered by geology, in studying the unceasing series of changes dependent on the circumstances of the time, as new conditions and new combinations successively arose in the course of the earth's long geological history, with constant variation in degree and intensity of action.

The Second Volume treats of the history of Strata, their appearance, conditions, and constitution having been described in Volume I. The succession of recognizable groups of Strata in different parts of the World, as at present known, is shown by several Tables in chapter i. The great geological systems or series, as defined by their relative unconformity, or differences of position, and by the organic remains peculiar to each, are then taken in hand, one after the other, from the oldest to the latest. Their fossils, whether of animal or vegetable origin, are carefully noted and often tabulated at some length. They are illustrated with many woodcuts and lithographic plates, all good artistic work, and all new except some borrowed from modern works on special groups and of great merit. The fossils figured have been selected with real scientific care, and some microzoa, not usually thought of so much as they should be as rock-makers, are introduced with good effect.

This volume rivals the first in the object of elucidating the History of the Earth; for, as that gave the physical or inanimate division of its history, this volume, enquiring in the first place what possibly may have been the original condition of the Earth's crust, enables us to note when Life first made its appearance upon it,—to determine the character of that Life, and to follow its development and successive modifications through all Geological Time.

Together with this study of Biological Evolution, the great physical changes of the surface, the constant alterations in the distribution of land and water, and the relation of these physiographic changes to the distribution of Life on the land and in the water are carefully noticed.

Besides the illustrations of fossils in Volume II. numerous diagrams of sections, views, plans, &c., as well as large maps enrich

each volume, and a full Index completes the work.

### XLIII. Intelligence and Miscellaneous Articles.

PHOTOGRAPHY OF THE LEAST REFRANGIBLE PORTION OF THE SOLAR SPECTRUM. BY J. C. B. BURBANK \*.

IT has been stated by eminent authorities that the process of staining dry plates with various dyes is not applicable to the photography of the invisible rays beyond the red of the solar spectrum. To test this question I have undertaken a series of experiments with the dye cyanine. This dye has of late come into considerable prominence in photography, owing to its orthochromatic effect when mixed with other dyes, such as chinoline-red,

azaline, erythrosine, and eosine.

It was discovered by Greville Williams, an Englishman, in 1861 but did not come into much prominence until the year 1884, when its usefulness as a sensitizer became more apparent. The dye is easily decomposed by light, and even in the dark both its solution and the plates coated with it are apt to become decomposed if kept for any length of time. Alone, it has been found very useful to sensitize plates for the orange and red portions of the spectrum. No experiments have to my knowledge been made upon the effect

of heat-rays upon cyanine plates.

The direct action of absorbents in the infra-red has not, hitherto, been tried with any success; moreover, it has been stated by so eminent an authority as Captain W. De W. Abney that it was impossible to make plates sensitive to any rays below the A of the solar spectrum by means of the addition of dyes to a film. It is true, however, that Major Waterhouse has succeeded by means of turmeric in obtaining evidence of the existence of a few lines on the less refrangible side of A, but in all cases except one these were reversed.

The plates employed were made by the M. A. Seed Co. of sensitometer 22. The method used in staining the plates and in the

<sup>\*</sup> From an advance proof from the 'Proceedings of the American Academy.' Communicated by the Author.

preparation of the dye is substantially the same as that employed

by J. B. B. Wellington,\* and is as follows.

Fifteen grains of cyanine are gently heated (over a steam bath) for from thirty to forty minutes in combination with 1 oz. of chloral hydrate and 4 oz. of water. The whole mixture should now be stirred vigorously. While this operation is going on, 120 grains of sulphate of quinine are dissolved by heat in a few ounces of methylated spirit. (If methylated spirit cannot be obtained, a solution of 90 per cent. alcohol and 10 per cent. wood spirits will answer perfectly well.) One ounce of strong aqua ammoniæ is now slowly added to the cyanine mixture above. Violent ebullition takes place immediately, chloroform being evolved, and cyanine deposited in a soluble form on the sides of the vessel. The mixture is allowed to settle for a few minutes, and then the supernatant liquid is decanted off very slowly, care being taken not to detach any of the cyanine that is formed on the sides.

To the remaining cyanine, three or four ounces of methylated spirit are added to dissolve it; the quinine solution is then added; and to the whole more methylated spirit, until the whole mixture measures from eight to nine ounces. This solution constitutes the "stock" solution, and should be kept away from all

light, as it is very apt to become decomposed.

All of the above operations should be conducted in as little light as possible. The following staining and drying processes should

be conducted in absolute darkness.

To thirty ounces of water are added  $1\frac{1}{2}$  drachms of the cyanine stock solution; the graduate that contained the cyanine is now washed out,  $1\frac{1}{2}$  drachms of strong aqua ammoniæ are added, and the whole mixture is stirred vigorously. Into this bath two or three plates, or half a dozen strips, can be dipped at once. They should be left there about four minutes; meanwhile the tray containing the plates should be rocked continuously, so as to insure a uniform action of the dye.

This bath, after having been used once, should be thrown away, as the action on a second batch of plates would be weak and imperfect. The plates can now be drained, dried, and used. While developing, I was careful to exclude all light whatever, although I think it possible that the plates may be developed safely in a dark greenish-yellow light. The developer used was a pyro-

and potash developer of (generally) normal strength.

In the first experiments the spectrum was produced by a Rowland flat diffraction-grating, mounted on a spectrometer-circle. This grating contained 17,000 lines to the inch. The observing-telescope of the spectroscope was replaced by a camera and lens.

Certain photographs were also taken by means of a Rowland concave grating of 14,500 lines to the inch, and of 21 ft. 6 in. radius of curvature. With this grating, the amount of light being less and the dispersion greater than in the former cases, the exposure had to be increased.

In all of the experiments ruby-red glass screens were used in

<sup>\*</sup> See Anthony Photographic Bulletin, December 24, 1887.

order to cut out all of the more refrangible part of the underlying spectrum. In some cases a weak solution of iodine in carbon

disulphide was used with good effect.

No difficulty was found in photographing from the A line to wave-length 9900, or to the limit assigned by Abney as the limit of the diffraction spectrum. None of the lines were reversed. A special study of the A group was made, photographs being taken at different seasons, in order to see if any changes in the remarkable group of lines constituting the A group could be noticed. No existing map represents this group correctly. Employing the second spectrum produced by a concave grating, 52 lines were observed between wave-lengths 7100 and 8000. In the same space Abney records only 24 lines. Between the head of A and the tail of A, the latter being the single line before the series of doublets begin which is so characteristic of the A group, my photographs show 17 lines. These photographs were taken in June between ten and one o'clock.

These results are of special interest when we consider that Abney has said in a Bakerian lecture, "As a result of these experiments I can confidently state that in no case did the addition of a dye cause any chemical effect to be produced by the rays below A of the solar spectrum, nor has Vogel claimed that they do."

It is interesting to note that Abney is led to believe that the photographic action, which has been noticed hitherto, by the use of dyes as sensitizers, can be attributed to a certain action of nitrate of silver on organic matter. This effect is a bleaching one, and only the more fugitive dyes can produce it. We are led to conclude from Abney's paper, that he believes that only a chemical effect produced in a specially prepared emulsion can be used to reproduce the infra-red rays. After many experiments he succeeded in producing such an emulsion. The colour of this verged upon the blue. Since the colour of plates stained with cyanine by the process I have described is also blue, there may be some physical significance in this resemblance.

My experiments show that a specially prepared emulsion is not necessary for the photography of the infra-red region. The chemical theory advanced by Abney, therefore, seems to need

revision.

## ON THE DISINTEGRATION OF IGNITED PLATINUM. BY H. KAYSER.

Attention has recently been again directed from various quarters to the phenomenon that ignited platinum throws off minute particles, and thus disengages dust, and this irrespective of how the ignition is produced, whether by the electrical current or by a flame. I wish to communicate a case of this kind, which has resulted in an important condition for the air-thermometer.

In the year 1885 I was engaged in determining the coefficient of expansion of air with the utmost accuracy, namely as a function

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of the pressure. I have been prevented by circumstances from completing this investigation. Very special care was devoted to the dryness of the air. For this purpose it passed through potash and sulphuric acid into a large glass receiver, the bottom of which was covered with anhydrous phosphoric acid; the air-thermometer was not filled with this until it had been stored for several days. The agreement between the coefficients with the various fillings was nevertheless insufficient; it varied for atmospheric

pressure between 3667 and 3676.

I imagined now that the air of the town might contain variable quantities of hydrocarbons; in order to eliminate this factor I passed the air through a hard-glass tube containing platinum wire, which was kept heated by a lamp placed underneath it. The air passed afterwards through caustic potash and sulphuric acid into the reservoir. When air was taken from this twenty-four hours afterwards the coefficient of tension was found to be 3731; air taken from the same reservoir six days afterwards, 3669. I then made several such determinations, of which I will mention one: the reservoir was filled after using the platinum wire; air removed twelve hours afterwards gave 3767, after three days 3673, and after six days 3670.

It appears thus that air which has passed over heated platinum has apparently a very high coefficient of tension, but after long standing it loses this property. This is explained by the fact that particles are detached from the platinum which are so small that they float for a long time in the air. They become coated by absorption with condensed layers of gas, which by heating in the air-thermometer are partially liberated. The value of the coefficient of tension thereby rises too high. But if the gas is at rest for some time, these particles settle down and the air is again pure.

If this explanation is correct, it must be possible by filtering the air to get at once the normal coefficient of tension. Hence, after passing the gas over the heated platinum through potash and sulphuric acid, I passed it through a layer of wool freed from fat, 15 centim. in length, which was so closely pressed that an excess of 20 centim. was necessary to drive the air through. After twelve hours the value 3670 was obtained, by which the explanation is

confirmed.—Wiedemann's Annalen, No. 7, 1888.

# ON FREEZING MIXTURES MADE WITH SOLID CARBONIC ACID. BY MM. CAILLETET AND E. COLARDEAU.

In a recent Note (Journal de Physik, vol. vii. p. 286) we gave the results of the comparison of various thermometric apparatus, and showed that they held to a temperature below  $-100^{\circ}$ .

The agreement in the indications of these instruments has led us to use the most sensitive of our thermoelectrical pincettes, graduated by direct comparison with the hydrogen-thermometer, to investigate the temperature of solid carbonic acid, either alone or mixed with various liquids.

In using carbonic acid snow to obtain intense cold it is usually mixed with ether, as directed by Faraday and Thilorier. In these conditions the ether is generally considered as intended to produce a much more intimate contact with the body to be cooled than is obtained with the snow alone.

It is, however, a question whether ether has not a special action

other than that.

We commenced by measuring the temperature obtained with carbonic acid snow alone. A thermoelectric pincette, by which a fraction of a degree could be estimated, was placed in the centre of a large mass of this substance. In some cases the snow was strongly compressed, and in others left to its ordinary porosity. The results obtained varied very slightly, and the temperature of the snow at the ordinary pressure is about  $-60^{\circ}$ .

To try what effect a vacuum has on the temperature, we used a Bianchi's rotatory air-pump and the absorbing action of potash; we were thus able to produce for some time together an almost complete vacuum; but although the experiment was frequently repeated, the conditions being varied as much as possible, the

temperature did not sink below  $-76^{\circ}$ .

The same thermoelectric pincette gave us in the pasty mixture of solid carbonic acid and ether a temperature of  $-77^{\circ}$  at the ordinary

pressure, and in a vacuum of about  $-103^{\circ}$ .

The following experiment shows very neatly the special part which ether plays. It is known that when a tube containing liquid carbonic acid is immersed in the mixture, the contents of the tube solidifies very rapidly. If the temperature of the mixture were not below that of the congelation of carbonic acid, this congelation

would not take place.

In order to ascertain the part played by the liquid in the mixture we gradually added carbonic acid to ether. The first portions of snow rapidly disappear in contact with the liquid. This disappearance is not solely due to a volatilization resulting from the difference of temperature, but to a solution of solid matter. For the ether, which has kept its transparency and limpidity, disengages carbonic acid steadily for a long time. By continuing the addition of the carbonic acid snow, a point is reached at which it ceases to dissolve, and the mixture then gradually becomes more and more pasty. By following the changes of temperature with the thermoelectric pincette, it will be observed that it sinks at each addition of snow until the liquid, losing its transparency, indicates that it is saturated.

It appears then natural to admit that the cold produced by solution of solid carbonic acid in ether is the cause of the difference of temperature observed between simple snow and the mixture.

greatest cold is attained just at the point of saturation.

It will be understood from this that if we vary the proportions of the mixture the differences of temperature should be almost null. provided there is an excess of solid snow which keeps up the saturation. We have found in fact that, by varying the proportions from a syrupy consistence almost to the state of solid, this difference

is scarcely 1°.

In order to confirm the part which we have ascribed to the ether we have made experiments with the following solvents. We have obtained the following results:—

	observed.
Chloride of methyle	82°
Sulphurous acid	
Acetate of amyle	-78
Terchloride of phosphorus .	-76
Bisulphide of carbon	
Absolute alcohol	
Chloride of ethylene	

With the last three liquids, and especially with chloride of ethylene, the solubility of carbonic snow is manifestly less than the others. These also are the liquids which produce least cooling.

By producing a vacuum over these liquids we can, as Faraday has shown, materially reduce the temperature, even below  $-100^{\circ}$ . With chloride of methyle and sulphurous acid it happens that this temperature in a vacuum is sufficiently low to solidify the solvent. All the mass then becomes solid, and from this point the temperature remains almost stationary.

The lowest temperature we have obtained under these conditions is with chloride of methyle. Solidification only takes place at

about —106°.

With chloroform, whose freezing-point is below that of carbonic acid, the action of the vacuum is not needed to produce this effect. Carbonic snow gradually added to the liquid dissolves at first with disengagement of carbonic acid. When the temperature has sunk to  $-77^{\circ}$  this ebullition ceases suddenly, and the whole mass solidifies. There is thus a freezing mixture which congeals under the influence of its own cooling.—Journal de Physique, September 1888.

# A SIMPLE PENDULUM EXPERIMENT TO EXPLAIN RESONANCE AND ABSORPTION. BY W. HOLTZ.

A caoutchouc tube is stretched between two door-posts by means of packthread attached to the ends, and nails. If two string pendulums are hung over this by means of hooks equidistant from the ends at about  $\frac{1}{6}$  of the width of the door, and if an impulse be given to one, the other is set in oscillations which increase as the others slacken. When the original one has come to rest the phenomenon is inverted. If the pendulums are unequal the second begins to vibrate indeed, but the vibrations do not continuously increase.—Beiblätter der Physik, No. 7, 1888.

### LONDON, EDINBURGH, AND DUBLIN

### PHILOSOPHICAL MAGAZINE

AND

### JOURNAL OF SCIENCE.

[FIFTH SERIES.]

#### NOVEMBER 1888.

XLIV. The Secular Annealing of Cold Hard Steel. By Carl Barus\*.

NASMUCH as the method I used for testing Maxwell's theory of the viscosity of solids contains a proof of that theory à fortion, I did not distinguish in my last papert between a break-up of configurations of molecular wholes and the more intensified break-up in which the integrity of the molecule itself is invaded. The experimental distinction is not always easy. If, for instance, I dissolve certain solids (pitch, say, in turpentine) I may produce a continuous series of viscous fluids; but the molecular mechanism by which this is brought about cannot in the present state of our knowledge of solution be said to be known. I may cite another striking example ebonite, which above 100° loses viscosity at an exceedingly rapid rate by mere heating; but, again, the molecular change which produces the viscous effect is obscure. And so generally in less remarkable experiments ‡. In the case of metals, it appears that those elements whose molecules are least stable and possibly monatomic § (K, Na, &c.) are of a soapy consistency, so that here viscosity ("Nachwirkung") and permanent set can hardly be distinguished. In general it appears that metallic permanent set is physical manifestation of looseness of molecular structure. If, as in the case of annealing glass-hard steel, the rigid arch (say) of molecular wholes breaks up because one or more of the molecules, the stones of

§ Ibid. chapter. xvi. § 308, &c.

Communicated by the Author.
 † This Magazine, August 1888.

<sup>†</sup> Cf. Lothar Meyer (Die modernen Theorien der Chemie, Breslau, 1884, chapter viii.), on solid molecular structure.

that arch, disintegrate, and if the decomposition be of a kind that the débris may be chemically recognized, then, by coordinating the viscous and the chemical observations, I obtain a fairly good notion of the molecular mechanism which has produced the viscous effect. This is the method I applied to prove Maxwell's theory. But partial disintegration or reconstruction of molecules may easily be conceived to occur in such a way as to escape detection altogether, or at least to escape detection as much as does a break-up of configurations of molecular wholes. It may, I think, be reasonably supposed that the solid molecule is of the form  $M_n$ , in which n is variable; and any given value of n will occur less frequently according as it is proportionately greater or less than the mean or typical value of n for the solid. The effect of strain, of change of strain, or even of long continued secular subsidence. is merely to vary the distribution of molecules  $M_n$ , so that the general properties of any observably finite part of the solid do not change\*.

I will adduce other points of view in succeeding papers; but the suggestions stated are sufficient, I think, to show the importance of discerning whether the cause of viscous deformation in tempered steel is the type of viscous deformation in general; or whether, in using the phenomena of annealing steel to test Maxwell's theory, I have merely interpreted the exception to prove the rule. The result of such an investigation, besides throwing light on the structure of solid matter, must ultimately lead to inferences bearing directly on the

questions of fusion, solution, and volatilization.

This inquiry being essentially a comparison of detail, will consume much time before it can be brought to an issue; and as the individual parts of my work have led to results which are of interest† apart from the purposes to which I hope ultimately to apply them, it is perhaps best to commu-

\* In other words, it is here supposed that the assumption of solid state has not thoroughly eliminated either the liquid or even the gaseous molecule; and that it has, on the other hand, produced molecules of an ultra-solid complexity. Here I touch the keynote of certain difficulties in my mind against conceiving the solid molecule as a uniformly distinct whole, capable of rotation (Kohlrausch viscosity), or capable of translation from strained to isotropic configuration (Maxwell viscosity). I look upon it as a more cumbersome thing, which may under favourable conditions even lose its identity, and which, when undergoing the motions stated, comes into serious conflict with contiguous molecules. Such a view, even if it be mere surmise (excepting the case of hard steel discussed) is a suggestive working hypothesis; for it seems broad enough to enable me to circumscribe the true phenomenon by clipping the postulate. This is the general endeavour of my present work.

† It is well known that experiments on the secular changes of metals are being made at Glasgow by Mr. Bottomley. Cf. Brit. Assoc. Report,

p. 537 (1888).

nicate the data separately. The following results on the secular annealing of cold glass-hard steel essentially sustain the inferences of my last paper. They were omitted because of the space occupied by the discussions there given. The rods to which the data refer are of Stubs's best steel, tempered in a special apparatus\*, by aid of which the wire heated to redness electrically is suddenly whipped into water. Freshly quenched samples of wire showed specific resistances (0° C.) as high as s=48. All the rods were tested for longitudinal uniformity of temper by stepping off, as it were, the resistance of lengths of 2 centim. each, for each of the consecutive 3 centim, of wire. The total length being about 25 centim., eight measurements were thus made. A device utilizing Matthiessen and Hoskin's method, and provided with a suitable rider, enabled me to do this with reasonable accuracy. Table I. contains the results as obtained with three batches of wire, of the diameters  $2\rho = 0.081$  centim., 0.044 centim., and centim. respectively. The approximate resistance (microhms) of the 2 centim. of length is designated by r.

Table I.—Longitudinal Uniformity of Temper of the Steel Rods. Variation from Mean, in terms of the Electrical Interval *Hard-soft*.

	ui 11u		• •						
No. 1. r=18500.	No. 2. 18500.	No. 3. 17700.	No. 4. 17600.		No. 6. 18500.	No. 7. 18400.	No. 8. 18500.	No. 9. 17400.	No. 10. 17900.
**************************************	- 002 - 2 - 2 - 2 - 6 - 2 10	- 13 - 4	- 2 - 2 - 2 - 7 - 2 - 6 - 2 3	$ \begin{array}{r}     \hline       010 \\       10 \\       - 7 \\       - 2 \\       6 \\       - 7 \\       - 11 \\       2 \end{array} $	- 005 - 3 - 7 5 - 1 - 2 - 7 9	-004 1 1 7 7 7 - 5 - 8 - 5	-009 - 11 - 11 - 3 - 3 5 5 1	-032 18 11 - 46 - 64 - 16 23 41	- 006 - 6 2 2 - 2 - 6 10 - 6
No. 11. r=61200.		No. 13. 61200.				No. 17. 6760.	No. 18. 6580.	No. 19. 7290.	No. 20. 6850.
-007 - 2 - 7 - 10 1 1 1 10	-·007 - 1 - 4 - 7 4 - 1 4 13	-·003 - 3 - 3 - 10 - 3 - 3 - 8 8	·023 - 1 1 - 7 - 4 - 4 - 4 - 4	- 016 - 1 - 3 - 9 - 12 - 12 - 1	- 006 - 2 3 - 2 - 2 - 2 - 2 - 3 7	*001 1 5 - 3 - 3 1 - 3 1	-009 7 15 3 - 1 11 - 5 - 20	·001 1 10 10 14 - 11 - 11 - 11	-·013 - 26 4 17 13 13 - 13 4

<sup>\*</sup> Bulletin U. S. Geological Survey, No. 14, p. 29 (1885). My present apparatus is horizontal in form, and enables me to quench the wires from any degree of red heat in water or other liquid at any desirable temperature.

With the exception of No. 9, the variations are, as a rule, well within one per cent, of the electrical value of the interval hard-soft. Where the resistance is larger or smaller than the mean value, it is possible that the parts were accidentally splashed by the water immediately before quenching, or quenched at a different degree of red heat. But inasmuch as the series of measurements for each rod takes some time, and as the effective resistances are necessarily small, I believe that the rods are even more homogeneous than Table I. indicates; for the errors introduced by variations of temperature, by the difficulty of clamping the thin, very brittle rods (soldering would change the temper enormously), and by other inconveniences of manipulation, are by no means negligible. Hence the degree of homogeneity found may be considered quite satisfactory.

In Table II. I give the mass m, length l, and density at 0° C.,  $\Delta_0$ , of some of the rods. The latter datum is essential for the determination of the sections. I shall also use it in the future in determining the secular volume-changes of these wires. Rods Nos. 11 to 15 are too thin for direct measurement. Hence a mean value of  $\Delta_0$  was here assumed. I may add that in the soft state the density of these rods is about

 $\Delta_0 = 7.80.$ 

TABLE II.—Mass Constants of the Glass-hard Steel Rods, June, 1885.

No.	m.	i.	$\Delta_0$ .	No.	m.	Z.	Δ <sub>0</sub> .
1	g. ·9910	centim.	g/cm <sup>8</sup> .	11	g. ·3257	centim. 27.94	$g/\mathrm{cm.}^{3}$
2	·9544	24·02	7·689	12	·3322	28·30	
3	·9970	25·25	7·703	13	·3170	27·20	
4	1·0483	26·30	7·705	14	·2888	24·35	
5	1·0079	25·46	7·703	15	·3004	26·07	
6	1.0243	25·80	7.687	16	2·4713	25·63	7·676
7	1.0089	25·47	7.670	17	2·4857	25·70	7·671
8	1.0074	25·50	7.682	18	2·1043	22·50	7·544
10	1·0666	26·68	7·726	19	2·5327	26·06	7·685
	1·0293	25·58	7·719	20	2·3557	24·40	7·653

Table III. contains the electrical constants of these rods;  $r_t$  being the observed resistance per centimetre, at  $t^{\circ}$ ,  $\alpha$  the temperature coefficient, and  $s_0$  the corresponding specific resistance at  $0^{\circ}$  C. The wires were quenched on June 1st and 2nd, 1885, and the measurements made at the time given, only a few days after hardening. Sections and radius are

given under q and  $\rho$  respectively. In most cases q is individually determined.

Table III.—Specific Resistance of the Glass-hard Steel Rods, measured June 4th and 8th, 1885.

(Effective length 20 centim. to 26 centim.)

No.	q×10 <sup>6</sup> .	$2\rho \times 10^3$ .	r <sub>t</sub> .	t.	$a \times 10^3$ .	_ 8 <sub>0</sub> .
	centim.2	centim.	microhm.	° C.		microhm.
1 2 3 4 5 6 7 8 9	5152 5168 5126 5173 5139 5165 5164 5143 5174 5214	80.6	9260 9250 8870 8810 8840 9260 9260 9260 8720 8950	27·5 27·8 28·3 27·0 27·2 26·8 27·0 26·3 26·3 25·1	1·5 1·6 1·6 1·6 1·5 1·5 1·5 1·5	46·0 46·0 43·7 43·8 43·7 46·1 45·8 46·0 43·6 45·1
11 12 13 14 15	1520 1520 1520 1520 1520 1520	}44	30670 30320 30620 30080 30990 3400	25·2 25·3 24·8 25·5 26·8	1.5 1.6 1.5 1.6 1.5	45·1 44·4 45·0 44·1 45·4 41·0
17 18 19 20	12610 12400 12650 12620	126.5	3382 4144 3643 3427	26·4 26·6 26·7 27·2	1·7 1·5 1·6 1·7	41·0 49·5 44·3 41·5

Finally, Table IV. contains the electrical constants of these rods made about 37 months after the first measurement. It also contains the variations,  $\Delta r_t$ , of the resistance per centimetre, as well as the variations,  $\Delta s_0$ , of the specific resistance. It will be seen that  $\Delta s_0$  is negative throughout, whereas the effect of atmospheric influence and the unavoidable abrasion in cleaning the surfaces of the wires before measurement, would produce a positive error. The same bridge and the same standards of German silver are used both in the measurements of Table III. and of Table IV. The fact that the wires differ in diameter, and therefore very largely in resistance, is a guarantee against the effect of differences of sectional errors of the bridge-wire. Again, although  $\Delta s_0$  is essentially the difference of secular change between the steel wire and the Germansilver standards, the fact that two standards (1.0 ohm and 0.1 ohm respectively) were used, at least partially eliminates the error due to variations in the standards. Moreover, the electrical effects of corresponding variations of temper (steel) and of the drawn strain which the German silver may possibly carry are enormously different. For instance, if glass-hard steel is boiled long enough the change of resistance may reach 12 per cent. and more. The effect of boiling German silver is of the order of some tenths per cent.\* Hence I apprehend no serious error in ascribing the whole of the observed variation of  $s_0$  in Table IV. to secular annealing of the glass-hard steel rods under experiment.

Table IV.—Specific Resistance of the Glass-hard Steel Rods, measured July 9th, 1888, and the Secular Variation. (q as in Table III.; effective length about 23 centim.)

No.	$2\rho \times 10^6$	$r_t$ .	t.	$\Delta r_t$ .	α×10 <sup>3</sup> .	s <sub>0</sub> .	Δε <sub>0</sub> .
	centim.	microhm.	° C.	microhm.		microhm.	microhm,
1 2 3 4 5 6 7 8 9 10	80.6	8460 8430 8010 7950 8010 8460 8400 8510 7920 8170	28	-790 -820 -860 -850 -830 -800 -800 -750 -800 -780	1.7	41·7 41·7 39·3 39·3 39·4 42·0 41·5 41·9 39·2 40·8	- 4·2 - 4·3 - 4·4 - 4·3 - 4·1 - 4·3 - 4·1 - 4·3 - 4·3
11 12 13 14 15	}44	27860 27710 28000 27490 28400	29	$\begin{array}{c} -2810 \\ -2610 \\ -2620 \\ -2590 \\ -2590 \end{array}$	1.7	40·5 40·3 40·7 40·0 41·3	- 4·6 - 4·2 - 4·3 - 4·1 - 4·1
16 17 19 20	126.5	2807 2807 2830 2808	29	- 590 - 570 - 810 - 620		33·3 33·4 33·8 33·5	- 7·7 - 7·5 -10·5 - 8·0

Summarizing the results of Tables III. and IV., it appears that during the 37 months between the two series of observations the specific resistance of the rods has fallen from 46.5 to 42.5 in case of the thin rods (diameter < 08 centim.), and from 43.7 to 35.4 in the case of the thicker rods (diameter 13 centim.). Hence the variations are a decrement of specific resistance amounting to some ten or even twenty per cent. in the extreme cases. This may be stated succinctly as follows:—mean atmospheric temperature acting on freshly

<sup>\*</sup> Cf. Bulletin U. S. G. S. No. 14, p. 94.

quenched steel for a period of years, produces a diminution of hardness about equal to that of 100° C. acting for a period Similar results have been suspected for magnetic measurements; but such results are very much less easily interpretable than the electrical data of Table IV. For earlier measurements \* prove conclusively that the electrical variations in question are sufficient evidence for the occurrence of concomitant changes of hardness, volume, carburation, &c. Finally, the above results show that the method of tempering magnets proposed by Dr. Strouhal and myself † warrants the steel against secular structural instability for a time certainly exceeding three years.

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XLV. Evidence of the Quantivalence of Oxygen derived from the Study of the Azo-Naphthol Compounds. By RAPHAEL Meldola, F.R.S., F.C.S., F.I.C., Professor of Chemistry in the City and Guilds of London Institute, Finsbury Technical College 1.

T has long been known that by the action of diazo-salts upon the naphthols and naphthylamines two parallel series of azo-derivatives are obtained which possess different characters according as they belong to the  $\alpha$ - or  $\beta$ -series. Thus the azo-derivatives of a-naphthol are distinctly phenolic in character, dissolving readily in alkalies and being thrown out again by acids in accordance with the general properties of all the oxyazo-compounds. Similarly, the azo-derivatives of  $\alpha$ naphthylamine have the general characters of true amidoazocompounds; the NH<sub>2</sub>-group, which they undoubtedly contain, can be readily diazotized, and by this means a series of secondary azo-compounds can be prepared. When the azo-derivatives of the  $\beta$ -series are compared with the corresponding  $\alpha$ -compounds marked differences are found to exist. These differences between the two classes of azo-compounds are too distinct to be attributed to the isomerism of position only—there are, in addition to such physical differences as those of melting-point and crystalline form, deeper-seated chemical distinctions which have suggested a different constitution for the two classes of compounds.

\* Cf. this Magazine, August. † Bull. U. S. G. S., No. 14, p. 171, 1885.

<sup>†</sup> Communicated by the Author, having been read at the Bath Meeting of the British Association, in connexion with the discussion on Valency.

With respect to the azo-derivatives of the  $\beta$ -series, with which I propose to deal in the present paper, the most striking feature is the greater stability and the insolubility in aqueous alkalies of the azo- $\beta$ -naphthol compounds, a character to which attention was first directed by Liebermann\* as the result of an observation made by Pfaff. So also the corresponding  $\beta$ -naphthylamine azo-derivatives differ from the  $\alpha$ -compounds in many particulars. The latter are distinctly basic and, as previously stated, are capable of being diazotized, these properties pointing to the presence of the NH2-group in the compounds in question. The  $\beta$ -derivatives, on the other hand. are less basic; they form salts only with great difficulty † and are diazotized with much less facility than the α-compounds 1. There are other points of difference between the two series to which attention may also be directed. Thus the a-naphthol azo compounds are readily alkylated &, while the corresponding B-naphthol derivatives can only be imperfectly alkylated |; the former can also be easily acetylated, while the latter require prolonged boiling with acetic anhydride and anhydrous sodium 'acetate ¶.

The first attempts to write the formulæ of the azo-compounds of the  $\beta$ -series on a different type to those of the  $\alpha$ -series were made by Liebermann\*\*, the author ††, and Zincke and Bindewald ‡‡. It is proposed now to consider briefly these different formulæ. The insolubility in alkalies of benzene-azo- $\beta$ -naphthol led Liebermann to the conclusion that this and analogous compounds no longer contained hydroxyl, and he suggested a formula which may be generalized as follows:-

$$C_{10}H_{6} \stackrel{\mathrm{NH}(\alpha)}{\bigcirc} N . X$$

[In this and succeeding formulæ X may stand for any The position of the azo-group (or its aromatic radical. representative) is in these compounds known to be in the aortho-position with respect to the other substituent.]

<sup>\*</sup> Ber. 1883, p. 2858.

<sup>†</sup> Zincke and Rathgen, Ber. 1886, p. 2482; Zincke and Lawson, Ber. 1887, p. 2896.

<sup>†</sup> Meldola, Journ. Chem. Soc., Trans. 1884, p. 117; Nietzki and Goll, Ber. 1886, p. 1281; Zincke and Lawson, Ber. 1887, p. 2896.

<sup>§</sup> Zincke and Bindewald, Ber. 1884, p. 3026.

Weinberg, Ber. 1887, p. 3171.

<sup>¶</sup> Meldola and East, Journ. Chem. Soc., Trans. 1888, p. 460.
\*\* Ber. 1883, p. 2858.

<sup>††</sup> Journ. Chem. Soc., Trans. 1884, p. 117.

<sup>‡‡</sup> Ber. 1884, p. 3026.

The formula proposed about the same time by the author for the β-naphthylamine azo-derivatives was analogous to Liebermann's, and was based on the assumption that the compounds in question no longer contained the NH<sub>2</sub>-group, because it was thought at the time that they were non-basic and could not be diazotized. The formula was written:—

$$C_{10}H_6 \stackrel{\mathrm{NH}}{\stackrel{(\alpha)}{\sim}} N . X$$

The observations which led Zincke to propose a modification of the above formula are as follows:—By the action of phenylhydrazine on  $\alpha$ -naphthaquinone a substance is obtained which is identical with that obtained by the action of diazobenzene salts on  $\alpha$ -naphthol. According to its mode of formation this substance may be either benzeneazo- $\alpha$ -naphthol (I.) or  $\alpha$ -naphthaquinone-hydrazone (II.) \*.

The last formula may, of course, be written on the ketone type of the quinone:—

$$\mathrm{C_{10}H_6} \overset{\mathrm{O}}{\swarrow}_{\mathrm{N.NH.C_6H_5}}$$

Which is the true formula of the compound in question does not appear to be decided by Zincke. In his first paper he suggests that the hydrazone is first formed and that this becomes transformed into the azo-compound by intramolecular change; but in his latest communication on this subject  $\dagger$  he appears to suggest that the substance may be capable of existing in both forms. With regard to the hydrazone of  $\beta$ -naphthaquinone, it has been found that this compound is isomeric and not identical with benzeneazo- $\beta$ -naphthol. Nevertheless Zincke regards both compounds as hydrazones, the isomerism being considered as the result of position only:—

<sup>\*</sup> This is the nomenclature recently proposed by E. Fischer, Ber. 1888, p. 984.
† Ber. 1888, p. 2202, note.

The analogy between the  $\beta$ -naphthol and  $\beta$ -naphthylamine azo-derivatives leads naturally to a corresponding formula for the latter:—

$$C_{10}H_6 \overset{N.\ NH.\ C_6H_5\dots(\alpha)}{\underset{NH.\dots\dots(\beta)}{\vee}} \ \ \mathrm{or} \ \ C_{10}H_6 \overset{N.\ NH.\ C_6H_5\dots(\alpha)}{\underset{NH.\dots\dots(\beta)}{\vee}}$$

Both this formula of Zincke's and that of the author indicate a relationship of the  $\beta$ -naphthylamine azo-derivatives to the azimido-compounds of Griess, as was first pointed out by the author in 1884 \*. These compounds would in fact be, according to this point of view, hydrazimides; and in apparent confirmation of this Zincke  $\dagger$  made the important discovery that these and other orthoamidoazo-compounds lost two atoms of hydrogen under the influence of oxidizing agents and gave rise to colourless products resembling the azimido-compounds in appearance and properties.

This account may be taken as a brief exposition of the views which have been, or are still held with respect to the constitution of these  $\beta$ -azo-compounds. In accordance with the suggested formulæ, these derivatives no longer contain hydroxyl or amidogen, and this is considered to account for the differences in character which have already been pointed out. According to the old view, the compounds in question would be formulated in the same manner as their  $\alpha$ -ana-

logues :-

$$C_{10}H_6$$
 $N=N \cdot X \dots (\alpha)$ 
 $C_{10}H_6$ 
 $N=N \cdot X \dots (\alpha)$ 
 $N=N \cdot X \dots (\alpha)$ 
 $NH_2 \dots (\beta)$ 

Although responsible in common with Liebermann for one of the first attempts to replace these older formulæ by symbolical expressions which appeared more in harmony with the then known properties of the compounds in question, it must be admitted that the experimental evidence acquired in more recent times does not bear out the view that amidogen and hydroxyl are absent. In the first place Nietzki and Goll ‡ found that, by means of the diazo-reaction, amidoazo- $\beta$ -naphthalene could be converted into the corresponding  $\beta$ -naphthol compound, *i. e.*,

$$C_{10}H_{6} \begin{array}{c} N_{2} \cdot C_{10}H_{7} \\ NH_{2}(\beta) \end{array} \quad into \qquad C_{10}H_{6} \begin{array}{c} N_{2} \cdot C_{10}H_{7} \\ OH(\beta) \end{array}$$

‡ Ber. 1886, p. 1281.

<sup>\*</sup> Journ. Chem. Soc., Trans. 1884, p. 116. † Ber. 1885, pp. 3134 & 3142.

In the next place Zincke and Lawson\* isolated the diazosalts of benzeneazo- $\beta$ -naphthylamine, and showed that these were decomposed quite normally by water into benzeneazo- $\beta$ -naphthol. Lastly, the author and F. J. East† showed that para- and meta-nitrobenzene-azo- $\beta$ -naphthylamine could be converted by means of nitrous acid in the presence of acetic acid into the corresponding  $\beta$ -naphthyl-acetates, *i.e.*,

into

Such facts as these point distinctly to the presence of a diazotizable  $NH_2$ -group; nevertheless the difficulty with which these compounds are diazotized and the instability of the diazosalts as compared with the  $\alpha$ -naphthylamine diazo-derivatives must be allowed due weight as evidence of a different constitution, a conclusion which is borne out by the formation of

oxidation-products of the azimido-type.

The evidence with respect to the absence of hydroxyl in the  $\beta$ -naphtholazo-derivatives has also of late been much weakened, if not altogether destroyed, by the results of Weinberg, Jacobson, and others. If the foregoing evidence of the presence of amidogen in the  $\beta$ -naphthylamine-azo-derivatives is considered conclusive, analogy leads to the conclusion that hydroxyl is present in the  $\beta$ -naphthol derivatives. The two groups of compounds are perfectly analogous and the latter can, as already stated, be obtained directly from the former by the replacement of NH2 by HO by the diazo-reaction. The presence of a replaceable hydrogen atom in benzeneazo-βnaphthol is shown by the fact that this compound can be ethylated by sodium ethylate and ethyl iodide f as well as by the fact that the said compound can be acetylated §. The mere fact of a replaceable hydrogen atom being present does not, however, give a decision in favour of either formula; the ethyl-derivative, for example, might be :-

† Journ. Chem. Soc., Trans. 1888, p. 464.

§ Meldola and East, loc. cit. p. 466.

<sup>\*</sup> Ber. 1887, p. 2896.

<sup>†</sup> Weinberg, Ber. 1887, p. 3171. A quantity of this ethyl derivative has been placed at the disposal of the author by Dr. Weinberg, and its products of reduction are being investigated in the laboratory of the Finsbury Technical College.

$$C_{10}H_6 \stackrel{1}{\stackrel{/}{\sim}} N \cdot N(C_2H_5) \cdot C_6H_5 \ (\alpha)$$

or

$$C_{10}H_{6} \sim N_{2} \cdot C_{6}H_{5} (\alpha)$$
 $C_{2}H_{5} (\beta)$ 

According to Weinberg, however, the product of reduction of this derivative is diamidoethoxynaphthylphenyl:—

$$\begin{array}{c} C_6H_4 \cdot NH_2 \dots (p) \\ NH_2 \dots (\alpha) \\ C_{10}H_5 & O.C_2H_5(\beta) \end{array}$$

From this result it appears that the ethyl is attached to the oxygen and that the second of the above formulæ is the correct one, or at any rate nearer the truth than the hydrazone-formula. So also the acetyl derivative might be written:—

$$C_{10}H_{6} \bigvee_{O \ (\beta)}^{N \ . \ N(C_{2}H_{3}O) \ . \ C_{6}H_{5}(\alpha)} \quad \text{or} \quad C_{10}H_{6} \bigvee_{O \ . \ C_{2}H_{3}O \ . \ (\beta)}^{N_{2} \ . \ C_{6}H_{5} \ . . . \ (\alpha)}$$

The products of reduction of this compound have not yet been completely examined; but if the first formula were correct acetanilide might be expected to be formed together with  $\alpha$ -amido- $\beta$ -naphthol. As far as the experiments have hitherto been taken it certainly appears that no acetanilide is among the products of reduction by stannous chloride. The hydrazone formula, both of the  $\beta$ -naphthol and  $\beta$ -naphthylamine azo-derivatives, would indicate that phenylhydrazine should be obtained from these compounds by reduction, but this has never been observed \*. Benzeneazo- $\beta$ -naphthol gives under these circumstances  $\alpha$ -amido- $\beta$ -naphthol and aniline, while benzeneazo- $\beta$ -naphthylamine gives aniline and  $\alpha\beta$ -naphthylene-diamine.

By heating benzeneazo- $\beta$ -naphthol with carbon disulphide to a high temperature, Jacobson obtained  $\dagger$  carbanilamido-naphthol and phenyl mustard-oil. The hydroxynaphthylmustard oil is first formed, and this becomes transformed into

the isomeric thiocarbamidonaphthol:

$$C_{10}H_6 \stackrel{OH}{\swarrow}_{N:CS} = C_{10}H_6 \stackrel{O}{\swarrow}_{N} C.SH$$

\* Zincke, Ber. 1885, p. 3134; Lawson, Inaug. Diss. Marburg, 1885, p. 11.
† Ber. 1888, p. 414.

The last compound then reacts with the residue, :N.  $C_6H_5$  to form carbanilamidonaphthol:—

$$C_{10}H_6\underbrace{\overset{O}{\underset{N}{\nearrow}}}C \cdot SH + : N \cdot C_6H_5 = C_{10}H_6\underbrace{\overset{O}{\underset{N}{\nearrow}}}C \cdot NH \cdot C_6H_5 + S$$

This result is considered by Jacobson to indicate the presence of hydroxyl in the azo-naphthol compound; but the evidence is not so satisfactory as could be desired, because the reaction takes place only at a high temperature (250°) in a sealed tube.

The most recent experimental evidence thus, on the whole, appears to favour a reversion to the old view of the constitution of the two groups of compounds; but the non-phenolic character of the azo-naphthol  $\beta$ -derivatives and the other differences pointed out are certainly not explained by the old formulæ.

In order to express the constitution of the azo- $\beta$ -naphthylamine compounds by a formula which meets all the requirements of the case, I have been led to the conclusion that the azo- and NH<sub>2</sub>-groups, being in the ortho-position, interact with the formation of a closed chain of nitrogen atoms:—

The formula of benzeneazo- $\beta$ -naphthylamine would, on this view, be written:—

$$C_{10}H_6$$
 $N$ 
 $N$ 
 $N$ 
 $C_6H_5$ 

That this formula is in harmony with the known properties of the substance will appear from the following considerations:—
The difficulty with which the compound forms salts may be explained by supposing that acids have first to break up the nitrogen ring, i. e.,

$$\begin{array}{cccc} -N & & -N & \\ -N & & \mathrm{into} & N \cdot \mathrm{C_6H_5} \\ H & & -\mathrm{NH_2 \cdot HCl} \end{array}$$

The same explanation may hold good with respect to the

difficulty of forming diazo-salts. When once diazotized this and analogous orthoamidoazo-compounds form tetrazo-salts, which differ in so many ways from the corresponding compounds of the para- or α-series that Zincke has suggested \* the closed chain formula:-

$$X'' \begin{picture}(20,0) \put(0,0){\line(1,0){100}} \put(0,0){\line(1,0)$$

It would be out of place here to discuss the evidence in favour of this formula, and I have only to express my concurrence therewith.

The relationship of orthoamidoazo-compounds to the azimides is shown at once by the formula now proposed. oxidizing agent simply removes the two H-atoms:—

These oxidized products are very stable and are not acted upon by reducing-agents, a fact also expressed by the formula. With reference to the azimides, theory indicates the existence of two isomeric series derived from

$$X'' \stackrel{N}{\underset{N}{\mid}} NH$$
 and  $X'' \stackrel{N}{\underset{NH}{\mid}} N$ 

The first of these formulæ was proposed by Griess for his azimido-compounds, and the second by Kekulé and Ladenburg for the same compounds. I have already given evidence to the effect that the latter is probably the correct formula †, a conclusion which has since been confirmed by Nölting and Abt‡. It follows, therefore, that Zincke's oxidized products are not true azimido-compounds, but belong to the isomeric series. If the said products were constructed on Kekulé's type, the orthoamidoazo-compounds would have the formula:—

$$X''$$
 $N-X'$ 
 $N$ 
 $N$ 

<sup>\*</sup> Ber. 1886, p. 1452.

<sup>†</sup> Phil. Mag. 1887, vol. xxiii. p. 525. ‡ Ber. 1887, p. 2999.

This view of their constitution is at once negatived by the fact that the azo-derivatives of  $\beta$ -naphthylamine all give  $\alpha\beta$ -naphthylene-diamine on reduction. This last property is, it is hardly necessary to say, expressed by the formula now

proposed.

Granting the probability of the latter, and, as has been shown, there is much to commend it to consideration, the analogy between the  $\beta$ -naphthylamine and  $\beta$ -naphthol derivatives, which has already been indicated, points to a similar constitution for the latter. I have no hesitation in proposing this modification of the generally received formula, although it will hardly find favour as yet with many chemists because it involves the existence in these compounds of tetravalent oxygen:—

$$C_{10}H_6 \bigvee_{0}^{N} N \cdot C_6H_5$$

There is no doubt, however, that the time is rapidly approaching when, in the opinion of the majority of workers, we shall have to give greater latitude to our notions of valency, both for elementary atoms and compound radicals. Without attempting here to discuss the general question, I may, however, point out that the higher valency of oxygen is only in accordance with what might be expected when we consider that in the periodic system this element is classed in a family of which the higher members are hexavalent\*. In the way of direct evidence that oxygen may be tetravalent, we have Friedel's compound formed by the combination of hydrogen chloride with dimethyl oxide†:—

$$\begin{array}{ccc} \mathrm{CH_3} \\ \mathrm{CH_3} \end{array} \hspace{-0.5cm} \hspace{-0.5c$$

All the facts and arguments in favour of the higher valency of oxygen have been recently brought together in two papers published by Mr. J. F. Heyes  $\ddagger$ . If this tetravalent function be conceded to oxygen, the properties of the azo- $\beta$ -naphthol compounds become easily explicable.

The first points requiring explanation from the present point of view are the identity of phenylhydrazone- $\alpha$ -naphthaquinone with benzeneazo- $\alpha$ -naphthal, and the non-identity of phenylhydrazone- $\beta$ -naphthaquinone with benzeneazo- $\beta$ -

<sup>\*</sup> See Lothar Meyer's 'Modern Theories,' Engl. ed. p. 342.

<sup>†</sup> Wurtz's 'Atomic Theory,' Int. Sci. Ser. p. 231. † Phil. Mag. 1888, vol. xxv. pp. 221 & 297.

naphthol. I am disposed to believe that all three substances are true azo-compounds and not hydrazones, the change in constitution resulting from the transfer of the H-atom, as suggested by Zincke in one of his earliest papers on this subject\*.

The arguments which tell against the hydrazone formula have already been stated. One other consideration here suggests itself. If the group: N. NH. X' were present in the  $\beta$ -azo-compounds, it might certainly be expected that if X' were made strongly acid by the introduction of NO2 or other acid radicals, the NH would become a salt-forming group, just as it is in the higher nitro-derivatives of diphenylamine, or in the acid diazoamido-compounds. But this is not the case; the nitrobenzeneazo-β-naphthols described by the author (Journ. Chem. Soc., Trans. 1885, pp. 661 & 668) are quite as insoluble in aqueous alkalies as benzeneazo-β-naphthol itself. The evidence in favour of such an intramolecular change as is required in the conversion of a hydrazone into an azo-compound has been accumulating since Zincke first put forward the suggestion. Thus Bernthsen found † that, by the action of phenylhydrazine upon acridyl-aldehyde, an azo-compound and not a hydrazone is formed. He suggests that the hydrazone undergoes intramolecular transformation, probably by the formation of an intermediate compound in accordance with the views of Victor Meyer:-

 $\begin{array}{c} C_{6}H_{5} . \ N[\overline{H}] - N : \mathrm{CH} . \ C_{13}H_{8}N = C_{6}H_{5} . \ N : N . \ \mathrm{CH}_{2} . \ C_{13}H_{8}N + H_{2}O. \\ |HO| \ \dot{H} \end{array}$ 

It must in future be recognized that the grouping

 $C_6H_5$ . NH. N: C:

may become transformed into C<sub>6</sub>H<sub>5</sub>. N:N.CH: The converse change is now known, through the researches of Japp and Klingemann<sup>‡</sup>, to take place in many reactions; *e. g.* the formation of phenylhydrazonepyruvic acid by the action of diazobenzene salts on ethylic sodiomethacetoacetate.

The formation of the benzeneazo-naphthols by the action of phenylhydrazine upon the quinones is therefore a reaction which has now found a parallel. Benzeneazo- $\alpha$ -naphthol is a true oxyazo-compound and requires no further consideration. The existence of two benzeneazo- $\beta$ -naphthols is, as shown by Zincke, due to position isomerism, only the formulæ would

\* Ber. 1884, p. 3026. † Ber. 1888, p. 743. † Proc. Chem. Soc. Dec. 15, 1887; Ber. 1887, pp. 3284 & 3398; Journ. Chem. Soc., Trans. 1888, p. 519. Also Victor Meyer, Ber. 1888, p. 11; and R. Meyer, Ber. 1888, p. 118.

be written, in accordance with the present suggestion, as follows:—

I. Produced by the action of diazobenzene salts on  $\beta$ -naphthol. II. Produced by the action of phenylhydrazine on  $\beta$ -naphthaquinone.

The proposed formulæ account for the formation of  $\alpha$ -amido- $\beta$ -naphthol and  $\beta$ -amido- $\alpha$ -naphthol respectively on reduction. The insolubility in alkali appears from the fact that the H-atom is not hydroxylic, but attached to an oxygen atom which forms part of a closed chain. This explains also why the  $\beta$ -azo-compounds are more stable, and are so much less readily alkylated or acetylated than the  $\alpha$ -derivatives.

The views which I have here advanced may be extended to all amidoazo- and oxyazo-compounds of the ortho-series. Thus the azo- $\beta$ -naphthol colouring-matters, the chrysoïdines, &c., may all be formulated on the types

or, in accordance with the ketonic quinone constitutional formula,

$$X \stackrel{N}{\swarrow} N \cdot Y$$
  $X \stackrel{N}{\swarrow} N \cdot Y$   $\dot{H}$ 

Whether these formulæ are accepted or not, the present discussion may serve to indicate the possibility of the existence of tetravalent oxygen in organic compounds, a possibility for which chemists have already been prepared from the inorganic side of their science. It remains to submit these views more fully to the test of experiment, and investigations in the direction indicated have for some time been in progress. I may point out, in conclusion, that the question is not without practical interest in addition to its scientific importance, since the majority of the azo-dyes now so largely used in the tinctorial industries belong to the  $\beta$ -series of naphthalene azo-derivatives.

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### XLVI. On the Reflexion and Refraction of Light. By Sir William Thomson\*.

1. GREEN'S doctrine † of incompressible elastic solid with equal rigidity, but unequal densities, on the two sides of an interface, to account for the reflexion and refraction of light, brings out, as is well known, for vibrations perpendicular to the plane of incidence (§ 12 below), exactly Fresnel's "sine-law:" and for vibrations in the plane of incidence a formula which agrees with Fresnel's tangent-law when the refractive index differs infinitely little from unity;—but which differs notably (enormously we may say) from it, and from the results of observation, in all practical cases:—in all cases, that is to say, in which the refractive index differs sufficiently from unity to have become subject of observation or measurement.

2. Since the first publication of Cauchy's work on the subject in 1830, and of Green's in 1837, many attempts have been made by many workers to find a dynamical foundation for Fresnel's laws of reflexion and refraction of light, but all hitherto ineffectually. On resuming my own efforts since the recent meeting of the British Association in Bath, I first ascertained that an inviscid fluid permeating among pores of an incompressible, but otherwise sponge-like, solid, does not diminish, but on the contrary augments, the deviation from Fresnel's law of reflexion for vibrations in the plane of incidence. Having thus, after a great variety of previous efforts which had been commenced in connexion with preparations for my Baltimore Lectures of this time four years ago, seemingly exhausted possibilities in respect to incompressible elastic solid, without losing faith either in light or in dynamics, and knowing that the condensational-rarefactional wave disqualifies ‡ any elastic solid of positive compressibility, I saw that nothing was left but a solid of such negative compressibility as should make the velocity of the condensationalrarefactional wave zero. So I tried it and immediately found that it, with other suppositions unaltered from Green's, exactly fulfils Fresnel's "tangent-law" for vibrations in the plane of incidence, and his "sine-law" for vibrations perpendicular to the plane of incidence. I then noticed that homogeneous air-less foam held from collapse by adhesion to a containing

<sup>\*</sup> Communicated by the Author.

<sup>†</sup> Camb. Phil. Soc. Dec. 1837. Green's Collected Papers, pp. 246, 258, 267, 268.

<sup>‡</sup> Green's Collected Papers, p. 246.

vessel, which may be infinitely distant all round, exactly fulfils the condition of zero velocity for the condensational-rarefactional wave; while it has a definite rigidity and elasticity of form, and a definite velocity of distortional wave, which can easily be calculated with a fair approximation to absolute accuracy.

absolute accuracy.

3. Green, in his original paper "On the Reflexion and Refraction of Light," had pointed out that the condensational-rarefactional wave might be got quit of in two ways, (1) by its velocity being infinitely small, (2) by its velocity being infinitely small, (2) by its velocity being infinitely great. But he curtly dismissed the former and adopted the latter, in the following statement:—"And it is not difficult to prove that the equilibrium of our medium would be unstable unless A/B > 4/3. We are therefore compelled to adopt the latter value of  $A/B^*$ ," ( $\infty$ ) "and thus to admit that in the luminiferous ether, the velocity of transmission of waves propagated by normal vibrations, is very great compared with that of ordinary light." Thus originated the "jelly" theory of ether, which has held the field for fifty years against all dynamical assailants, and yet has failed to

make good its own foundation.

4. But let us scrutinize Green's remark about instability. Every possible infinitesimal motion of the medium is, in the elementary dynamics of the subject, proved to be resolvable into coexistent condensational-rarefactional wave-motions. Surely, then, if there is a real finite propagational velocity for each of the two kinds of wave-motion, the equilibrium must be stable! And so I find Green's own formula proves it to be provided we either suppose the medium to extend all through boundless space, or give it a fixed containing vessel as its boundary. If, left to itself in space, there be a bubble of air contained in the ordinary film, in which we suppose the tension to be constant however much it may expand or shrink, it will come to stable equilibrium in the form of a globe of such size that the pressure inwards on the air due to the tension of the film is equal to the air-pressure outwards. But if instead of being constant, the tension of the film varies as  $t^{1-\kappa}$  (t denoting its thickness) the equilibrium will be stable ‡ or unstable according as  $\kappa$  is positive or negative. A finite

<sup>\*</sup> A and B are the velocities of the condensational and distortional waves respectively; suppose for a moment the density of the medium units.

<sup>†</sup> Collected Papers, p. 253; formula (C).

<sup>‡</sup> Provided instability of the film itself (by thicker parts having greater contractile force than thinner parts) is artificially guarded against by keeping it arbitrarily of uniform thickness.

portion of Green's homogeneous medium left to itself in space will have the same kind of stability or instability according as A/B > 4/3, or A/B < 4/3. In fact  $A = \frac{4}{3}B$ , in Green's notation, is what I have called the "bulk-modulus" of elasticity\*, and denoted by k (being infinitesimal change of pressure divided by infinitesimal change from unit volume produced by it: or the reciprocal of what is commonly called "the compressibility"). B is what I have called the "rigidity," as an abbreviation for "rigidity-modulus," and which we may regard as essentially positive. Thus Green's limit A/B > 4/3 simply means positive compressibility, or positive bulk-modulus: and the kind of instability that deterred him from admitting any supposition of A/B<4/3 is the spontaneous shrinkage of a finite portion if left to itself in a volume infinitesimally less, or spontaneous expansion if left to itself in a volume infinitesimally greater, than the volume for equilibrium. This instability is, in virtue of the rigidity of the medium, converted into stability by attaching the bounding surface of the medium to a rigid containing vessel. How much smaller than 4/3 may A/B be we now proceed to investigate, and we shall find, as we have anticipated, that for stability it is only necessary that A be positive.

5. Taking Green's formula (C), but to make the energy principle which it expresses clearer (he had not even the words "energy," or "work"!), let W denote the quantity of work required per unit volume of the substance, to bring it from its unstressed equilibrium to a condition of equilibrium in which the matter which was at (x, y, z) is at (x+u, y+v, z+w), u, v, w being functions of x, y, z such that each of the nine differential coefficients du/dx, du/dy, ... &c. is an infinitely small numeric, we have

$$W = \frac{1}{2} \left\{ A \left[ \left( \frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} \right)^2 + B \left[ \left( \frac{dw}{dy} + \frac{dv}{dz} \right)^2 + \left( \frac{du}{dz} + \frac{dw}{dx} \right)^2 + \left( \frac{dv}{dx} + \frac{du}{dy} \right)^3 \right] - 4B \left( \frac{dv}{dy} \frac{dw}{dz} + \frac{dw}{dz} \frac{du}{dx} + \frac{du}{dx} \frac{dv}{dy} \right) \right\} \qquad . \qquad (1).$$

This, except difference of notation, is the same as the formula

\* 'Encyclopedia Britannica,' Article "Elasticity,": reproduced in Vol. III. of my Collected Papers, soon to be published.

for energy given in Thomson and Tait's 'Natural Philosophy,'

§ 693 (7).

6. To find the total work required to alter the given portion of solid from unstrained equilibrium to the strained condition (u, v, w) we must take  $\iiint dx \, dy \, dz$  W throughout the rigid containing vessel. Taking first the last line of (1); integrating the three terms each twice successively by parts in the well-known manner, subject to the condition u=0, v=0, w=0 at the boundary; we transform the factor within the last vinculum to

$$\iiint dx\,dy\,dz\,\bigg(\frac{dv}{dz}\frac{dw}{dy}+\frac{dw}{dx}\frac{du}{dz}+\frac{du}{dy}\frac{dv}{dx}\bigg).$$

Adding this with its factor -4B to the other terms of (1) under  $\iiint dx \, dy \, dz$ , we find finally

$$W = \frac{1}{2} \iiint dx \, dy \, dz \, \left\{ A \left( \frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} \right)^2 + B \left[ \left( \frac{dw}{dy} - \frac{dv}{dz} \right)^2 + \left( \frac{du}{dz} - \frac{dw}{dx} \right)^2 + \left( \frac{dv}{dx} - \frac{du}{dy} \right)^2 \right] \right\} . (2).$$

This shows that positive work is needed to bring the solid to the condition (u, v, w) from its unstrained equilibrium and therefore its unstrained equilibrium is stable, if A and B are

both positive, however small be either of them.

7. If A=0, as we are going to suppose it for our optical problem, no work is required to give the medium any infinitely small irrotational displacement; and thus we see the explanation of the zero-velocity of the condensational and rarefactional wave which Green notices as corresponding to the case of A=0. But for present convenience, and until the Aberration of Light, or, generally, the motion of ponderable bodies through ether and related questions of electrostatics, electric currents, and magnetism, come to be considered in connexion with conceivable qualities of the luminiferous ether, we shall suppose forces proportional to cubes of strains to act in such a manner as to render stable the equilibrium which is neutral or "labile" with no other forces acting than those taken into account in (1) and (2) above. Accordingly, as a

<sup>\*</sup> This word, very well chosen as it seems to me, has I believe been, by some French writers, employed to signify such equilibrium as that of a rigid body on a perfectly smooth horizontal plane, or of water in a rigid closed vessel entirely filled by it.

second approximation, correcting (1) and (2) in which only forces in simple proportion to strains are taken into account, we may now have, for the case of A=0,

$$W = \frac{1}{2} \iiint dx \, dy \, dz$$

$$\left\{ B \left[ \left( \frac{dw}{dy} - \frac{dv}{dz} \right)^2 + \left( \frac{du}{dz} - \frac{dw}{dx} \right)^2 + \left( \frac{dv}{dx} - \frac{du}{dy} \right)^2 \right] + I_4 \right\} . (3),$$

where  $I_4$  denotes an essentially positive homogeneous function of the fourth degree of  $\frac{du}{dx}$ ,  $\frac{du}{dy}$ , ...  $\frac{dv}{dx}$ , ...  $\frac{dw}{dy}$ ,  $\frac{dw}{dz}$ , isotropic

relatively to (x, y, z).

8. The equations of motion of the general elastic solid, taken direct from the equations of equilibrium\*, are, in terms of our previous notation adopted from Green, and with  $\zeta$  to denote density,

$$\left\{ \frac{d^{2}u}{dt^{2}} = \frac{dP}{dx} + \frac{dU}{dy} + \frac{dT}{dz}, \right\}$$

$$\left\{ \frac{d^{2}v}{dt^{2}} = \frac{dU}{dx} + \frac{dQ}{dy} + \frac{dS}{dz}, \right\}$$

$$\left\{ \frac{d^{2}w}{dt^{2}} = \frac{dT}{dx} + \frac{dS}{dy} + \frac{dR}{dz}, \right\}$$

$$\left\{ \frac{d^{2}w}{dt^{2}} = \frac{dT}{dx} + \frac{dS}{dy} + \frac{dR}{dz}, \right\}$$
(4),

where u, v, w denote (as above from Green) displacements, not velocities; P, Q, R, normal components of pull (per unit area) on interfaces respectively perpendicular to x, y, z; and S, T, U respectively the tangential components of pull as follows:—

$$S \begin{cases} = \text{ pull parallel to } y \text{ on face perpendicular to } z, \\ = & ,, & , & z & , & , & , & y, \\ T \begin{cases} = & ,, & ,, & z & ,, & ,, & x, \\ = & ,, & ,, & z & ,, & ,, & x, \\ = & ,, & ,, & z & ,, & ,, & ,, & z, \\ \end{bmatrix} . (5).$$

$$U \begin{cases} = & ,, & ,, & z & ,, & ,, & ,, & z, \\ = & ,, & ,, & z & ,, & ,, & ,, & z, \\ = & ,, & ,, & z & ,, & ,, & ,, & z, \\ = & ,, & ,, & ,, & ,, & ,, & ,, & z, \\ \end{bmatrix} . (5).$$

9. For an isotropic solid, using Green's notation A, B as above (§ 3), we have†

<sup>\*</sup> Thomson and Tait, 'Natural Philosophy,' § 697.
† Thomson and Tait, 'Natural Philosophy,' § 693 and § 670 (6).

$$S = B\left(\frac{dw}{dy} + \frac{dv}{dz}\right); \quad T = B\left(\frac{du}{dz} + \frac{dw}{dx}\right), \quad U = B\left(\frac{dv}{dx} + \frac{du}{dy}\right). \quad (6);$$

$$P = A\delta - 2B\left(\frac{dv}{dy} + \frac{dw}{dz}\right); \quad Q = A\delta - 2B\left(\frac{dw}{dz} + \frac{du}{dx}\right);$$

$$R = A\delta - 2B\left(\frac{du}{dx} + \frac{dv}{dy}\right). \quad (7),$$

where

Using these in (4) we find, as the equations of motion,

$$\zeta \frac{d^2 u}{dt^2} = (\mathbf{A} - \mathbf{B}) \frac{d\delta}{dx} + \mathbf{B} \nabla^2 u \; ; \quad \zeta \frac{d^2 v}{dt^2} = (\mathbf{A} - \mathbf{B}) \frac{d\delta}{dy} + \mathbf{B} \nabla^2 v \; ;$$
$$\zeta \frac{d^2 w}{dt^2} = (\mathbf{A} - \mathbf{B}) \frac{d\delta}{dz} + \mathbf{B} \nabla^2 w \quad . \quad (9),$$

where

$$\delta = \frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} \quad . \quad . \quad . \quad (10),$$

and

$$\nabla^2 = \frac{d^3}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \quad . \quad . \quad . \quad (11).$$

10. From (9) we find, by taking d/dx of the first, d/dy of the second, and d/dz of the third, and adding,

$$\mathbf{\zeta} \frac{d^2 \delta}{dt^2} = \mathbf{A} \nabla^2 \delta \quad . \quad . \quad . \quad . \quad (12).$$

Put now

$$u'=u-\frac{d}{dx}\nabla^{-2}\delta$$
;  $v'=v-\frac{d}{dy}\nabla^{-2}\delta$ ;  $w'=w-\frac{d}{dz}\nabla^{-2}\delta$  (13);

which implies

$$\frac{du'}{dx} + \frac{dv'}{dy} + \frac{dw'}{dz} = 0 \quad . \quad . \quad (14)$$

and we find, by (9),

$$\zeta \frac{d^2 u'}{dt^2} = B \nabla^2 u'; \quad \zeta \frac{d^2 v'}{dt^2} = B \nabla^2 v'; \quad \zeta \frac{d^2 w'}{dt^2} = B \nabla^2 w' \quad . \quad (15).$$

Equations (12), (14), and (15) prove the footnote to § 3: and they prove, further, that any infinitesimal disturbance whatever is composed of specimens of the condensational-rarefactional wave, and specimens of the distortional wave, coexisting: and, lastly, they prove that the displacement in

the condensational-rarefactional wave is irrotational, because we see by (13) that an absolutely general expression for its components, u-u', v-v', w-w', if denoted by u'', v'', w'', is

$$u'' = \frac{d\Psi}{dx}, \quad v'' = \frac{d\Psi}{dy}, \quad w'' = \frac{d\Psi}{dz} \quad . \quad . \quad (16),$$

where  $\Psi$  is any function such that

$$\nabla^2 \Psi = \delta$$
 . . . . . (17).

Hence, as  $\delta$  satisfies (12), we have

$$\xi \frac{d^2 \Psi}{dt^2} = A \nabla^2 \Psi \quad . \quad . \quad . \quad (18);$$

and we see, finally, that the most general solution of the equations of infinitesimal motion is given by

$$u=u'+u''$$
,  $v=v'+v''$ ,  $w=w'+w''$ , . . (19):

provided u', v', w' satisfy (14) and (15); and u'', v'', w''

satisfy (16) and (18).

11. Let us now work out the general problem of reflexion and refraction between two portions of homogeneous elastic solid sliplessly attached to one another at a plane interface, and having different densities,  $\xi$ ,  $\xi$ ,; different rigidities, B, B,; and different values, A, A,, for the condensational-rarefactional wave modulus. Thus, if  $\alpha$ ,  $\beta$ ;  $\alpha$ ,  $\beta$ , denote the velocities of the condensational-rarefactional, and of the distortional, waves respectively in the two mediums, we have

$$\alpha = \sqrt{(A/\zeta)}, \quad \alpha_i = \sqrt{(A/\zeta_i)}$$

$$\beta = \sqrt{(B/\zeta)}, \quad \beta_i = \sqrt{(B/\zeta_i)}$$

$$\} \quad . \quad . \quad (20).$$

To avoid circumlocutions we shall suppose the interface horizontal, and call the two mediums, or solids, the upper and the lower respectively. Take OX vertically upwards; and OY horizontal to the right: and let the incident ray come from the left obliquely downwards, in the plane YOX; so that, if i denote the angle of incidence, the equation of the wave-front of the incident ray is

$$x\cos i + y\sin i = \text{const.}$$

12. Consider first the case of vibrations perpendicular to the plane of incidence. The medium being isotropic, no condensational waves can be generated at the interface. There is therefore just one reflected and one refracted ray; all vibrations are perpendicular to the plane of incidence; and all three waves are purely distortional. It is clear also that

the phases of all the three waves must agree at the interface. Thus if, to express the disturbance in the lower medium, we take

$$w = \sin(\omega t + l_i x + m_i y), (x \text{ negative})$$
 . . . (21),

where

$$l_i = \cos i_i \omega / \beta_i, \quad m_i = \sin i_i \omega / \beta_i \quad . \quad . \quad (22),$$

i, denoting the angle of refraction; we must have, for the disturbance in the upper medium,

$$w = f\sin(\omega t + lx + my) + g\sin(\omega t - lx + my), (x \text{ pos.})$$
(23),

where

$$l = \cos i \omega / \beta$$
,  $m = \sin i \omega / \beta$  . . . (24).

The agreement of phases all along the interface, that is for all values of y, requires

$$m=m_{i}$$
;

and therefore, by (22) and (24),

$$\sin i/\beta = \sin i/\beta, \quad . \quad . \quad . \quad (25),$$

which proves the "law of refraction." It, with (22) and (24), gives

 $l = m \cot i; \quad l_i = m \cot i, \quad . \quad . \quad (26).$ 

The other interfacial conditions are simply w continuous; and  $[\S 9, (6)]$  T, continuous; which give

$$f+g=1$$
; and  $Bl(f-g)=B_{i}l_{i}$  . . . (27);

whence

$$f = \frac{1}{2} \frac{Bl + B_i l_i}{Bl}$$
;  $g = \frac{1}{2} \frac{Bl - B_i l_i}{Bl}$  . . . (28);

$$\frac{g}{f} = \frac{\mathrm{B}l - \mathrm{B}_{l}l_{l}}{\mathrm{B}l + \mathrm{B}_{l}l_{l}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (29).$$

In the case of equal rigidities, or B=B, this becomes

$$\frac{g}{f} = \frac{l - l_{\prime}}{l + l_{\prime}} = \frac{\cot i - \cot i_{\prime}}{\cot i + \cot i_{\prime}} = -\frac{\sin (i - i_{\prime})}{\sin (i + i_{\prime})} \quad . \quad (30),$$

which is Fresnel's "sine-law."

13. In the more difficult case of vibrations in the plane of incidence, we have two displacement-components, u, v, to consider, instead of only the one, w; and two surface-pull components, P and U, instead of the one, T: and our interfacial conditions now are u, v, P, U all continuous.

We have now condensational-rarefactional waves, besides distortional waves, to deal with: and it is therefore convenient to divide the solution according to (19); and, as a twodimensional solution of (14), to take

Thus we have

$$u = \frac{d\phi}{dy} + \frac{d\psi}{dx}; \quad v = -\frac{d\phi}{dx} + \frac{d\psi}{dy} \quad . \quad . \quad (32);$$

which, by (6) and (7), give

$$P = 2B \frac{d^2 \phi}{dx dy} + \left(-2B \frac{d^2}{dy^2} + A \nabla^2\right) \psi;$$

$$U = B \left[ \left( \frac{d^2}{dy^2} - \frac{d^2}{dx^2} \right) \phi + 2 \frac{d^2 \psi}{dx dy} \right]$$
(33).

We may now, to represent the two refracted waves, assume, in the lower medium,

$$\phi = \sin(\omega t + l_i x + my)$$
;  $\psi = C_i \sin(\omega t + \lambda_i x + my)$ . (34); and to represent the incident wave, supposed distortional, and the two reflected waves, in the upper medium

$$\phi = F \sin(\omega t + lx + my) + G \sin(\omega t - lx + my);$$
  
$$\psi = C \sin(\omega t - \lambda x + my) . \quad (35),$$

where  $l, l_{j}$ , and m, still given by (22) and (24), verify (15), which give

$$\zeta\omega^2 = B(l^2 + m^2)$$
; and  $\zeta_i\omega^2 = B_i(l_i^2 + m^2)$ . (36); and similarly,  $\lambda$ ,  $\lambda_i$ , according to (18), are given by

$$\zeta\omega^2 = A(\lambda^2 + m^2); \quad \zeta_{,\omega}^2 = A_{,(\lambda_{,}^2 + m^2)}.$$

Also, if by j and j, we denote the angles of reflexion and refraction of the condensational-rarefactional waves, we have, similarly to (25), (26),

$$\sin j/\alpha = \sin j_1/\alpha_1 = \sin i/\beta$$
;  $\lambda = m \cot j$ ;  $\lambda_1 = m \cot j$ . (38).

14. The continuity of u, v, P, U, on the two sides of the interface, gives, by (32), (33), (34), (35);

$$-l(F-G)+mC=-l_1+mC_1$$
 . . . . . . (40);

$$-Blm(F-G) + [Bm^{2} - \frac{1}{2}A(\lambda^{2} + m^{2})]C$$

$$= -B_{l}lm + [B_{l}m^{2} - \frac{1}{2}A_{l}(\lambda_{l}^{2} + m^{2})]C_{l}. \quad (41);$$

$$B\{(l^2-m^2)(F+G)+2\lambda mC\}=B_l(l_l^2-m^2-2\lambda_l mC_l) \qquad (42).$$

Eliminating (F+G) from (39) and (42); and (F-G) from (40), (41) we find two equations for C and  $C_I$ ; and then (39), (40) give (F+G), (F-G); and thus we find our four unknown quantities. The resulting formulas are greatly simplified by the assumption of equal rigidities  $(B=B_I)$  adopted by Green on account of its simplicity, and proved by Lorentz and Rayleigh to be necessary, in the incompressible-solid theory, to get any approach to agreement with observation. It seems equally, or almost equally, necessary in the other extreme form of the elastic solid theory which I am now suggesting; but at all events I adopt it for the present on account of its simplicity. It gives, by the elimination of (F-G) from (40) and (41),

$$A(\lambda^{2} + m^{2})C = A_{i}(\lambda_{i}^{2} + m^{2})C_{i} . . . . (43),$$

or, by (37), 
$$\zeta C = \zeta_i C_i \ldots \ldots \ldots \ldots \ldots (44)$$

whence, by elimination of (F+G) from (39) and (42), and by (37),

$$\frac{\lambda C + \lambda_i C_i}{m} = \frac{l_i^2 + l^2}{l^2 + m^2} = \frac{\zeta_i - \zeta}{\zeta} \quad . \quad . \quad (45) ;$$

whence

$$C = m \frac{\zeta_i}{\zeta} \frac{\zeta_i - \zeta}{\zeta_i \lambda + \zeta \lambda_i}; \quad C_i = m \frac{\zeta_i - \zeta}{\zeta_i \lambda + \zeta \lambda_i} \quad . \quad . \quad (46).$$

This, used in (40), and (45) in (39), give

$$\mathbf{F} - \mathbf{G} = \frac{l_I}{l} + \frac{m^2(\zeta_I - \zeta)^2}{l(\zeta_I \lambda + \zeta \lambda_I)\zeta} \quad . \quad . \quad . \quad . \quad (47) ;$$

These (46), (47), (48), with (34), (35), and (32), express the

complete solution of our problem.

15. To interpret it remark that (32) represent the components of three distinct waves in the upper medium, and two in the lower, of which the directions of propagation make angles with the normal to the interface equal respectively to  $i, j, i_n, j_i$ ;  $[(j, i_n, j_i)$  being given in terms of i by (25) and (38)]; and of which the amplitudes are as follows:—

incident wave (distortional) . . . . . .  $\omega \cdot F/\beta$  distortional reflected wave . . . .  $\omega \cdot G/\beta$  condensational-rarefactional reflected wave .  $\omega \cdot C/\alpha$  distortional refracted wave . . . .  $\omega \cdot 1/\beta$  condensational-rarefactional refracted wave .  $\omega \cdot C/\alpha$   $\omega \cdot C/\alpha$   $\omega \cdot C/\alpha$ 

16. To verify that the sum of the activities (rates of doing work per unit of time) of the four reflected and refracted waves is equal to the activity of the incident wave, consider pencils of them, all cutting the interface in a square with its sides respectively perpendicular and parallel to the plane of incidence. The activity of each of these pencils is equal to twice the kinetic energy in a length of it equal to its wavelength, divided by the common period; or, which is the same, twice its kinetic energy per unit volume, multiplied by its sectional area, multiplied by its propagational velocity. Now twice the kinetic energy per unit volume of a wave of either species in an elastic solid is equal to the density of the solid, multiplied by half the square of the maximum molar velocity; and the sectional areas of our five pencils are respectively  $\cos i$ ,  $\cos j$ ,  $\cos j$ ,  $\cos j$ . Thus the activity of the incident pencil, for example, is

or, by (24),  $\zeta \cdot \frac{1}{2} \omega^4 (F/\beta)^2 \cos i\beta \cdot \ldots \cdot (50);$   $\frac{1}{2} \omega^3 \zeta F^2 l \cdot \ldots \cdot \ldots \cdot (51);$ 

and is similarly found for the others. Hence the activities of the five pencils, each divided by  $\frac{1}{2}\omega^3$ , are respectively

$$\zeta F^2 l$$
 ... incident (distortional) . . . . . (52);

$$\zeta G^2 l$$
 . . . distortional reflected . . . . . (53):

$$\xi_i l_i$$
 . . . distortional refracted . . . . . (54);

$$\zeta$$
C<sup>2</sup>  $\lambda$  . . . condensational-rarefactional reflected (55);

$$\xi_i C_i^2 \lambda_i$$
... condensational-rarefactional refracted (56).

17. The first of these must be equal to the sum of the other four, and thus, subtracting from each side the second, we find, as a form of the equation of energies,

$$\zeta l (\mathbf{F} + \mathbf{G})(\mathbf{F} - \mathbf{G}) = \zeta_l l_l + \zeta C^2 \lambda + \zeta_l C_l^2 \lambda_l \qquad (57),$$

which is verified by (47), (48), and (46). In verifying it we find, from (46),

$$\zeta C^2 \lambda + \zeta_i C_i^2 \lambda_i = m^2 \frac{\zeta_i}{\zeta} \frac{(\zeta_i - \zeta)^2}{\zeta_i \lambda + \zeta \lambda_i} . \qquad (58)$$

which is an important expression for the sum of the energies carried away per unit of time by the reflected and refracted condensational-rarefactional waves. In using these results, (52)...(58), it is convenient to remark that, by (24), (22), (38), we have

$$l = \frac{\omega}{\beta} \cos i; \quad m = \frac{\omega}{\beta} \sin i; \quad l_i = \frac{\omega}{\beta_i} \left( 1 - \frac{\beta_i^2}{\beta^2} \sin^2 i \right)^{\frac{1}{2}} \quad . \quad (59);$$

$$\lambda = \frac{\omega}{\alpha} \left( 1 - \frac{\alpha^2}{\beta^2} \sin^2 i \right)^{\frac{1}{2}}; \quad \lambda_i = \frac{\omega}{\alpha_i} \left( 1 - \frac{\alpha_i^2}{\beta^2} \sin^2 i \right)^{\frac{1}{2}} \quad . \tag{60};$$

18. When  $\alpha$  and  $\alpha$ , are small in comparison with  $\beta$ , we have, approximately,

$$\lambda = \omega/\alpha$$
;  $\lambda_i = \omega/\alpha_i$ ;

and (58), and (52) with (47) (48), become approximately

$$\frac{\alpha}{\beta}\sin^2 i \, \frac{\zeta_I}{\zeta^2} \, \frac{(\zeta_I - \zeta)^2}{\zeta_I + \zeta_A/\alpha_I} \, \frac{\zeta_\omega}{\beta} \, \dots \, (62),$$

and

$$\frac{1}{4} \sec i \left( \frac{\beta}{\beta_i} \cos i_i + \frac{\beta^2}{\beta_i^2} \cos i \right)^2 \frac{\zeta \omega}{\beta} . \quad (63);$$

which show that the energy carried away by the reflected and refracted condensational-rarefactional waves (62) is very small in comparison with the activity (63) of the incident distortional wave, whatever the angle of incidence. It is to be remarked that the wave-length of the condensational-rarefactional wave, in the upper medium for example, is  $\alpha/\beta$  of the wave-length of the distortional wave, while, as we see by (61),  $(4\tilde{6})$ , (47), (48), their amplitudes of vibration are comparable. Hence if we suppose  $\alpha/\beta$  infinitely small, we must suppose the ratio of the vibrational amplitude of the incident wave to its wave-length to be infinitely small in comparison with  $\alpha/\beta$ , in order that our formulas may still hold, or, which is the same, in order that the condensations and rarefactions may be infinitely small.

19. Without further preface, let A=0; which makes  $\alpha=0$ ; and  $\lambda = \infty$ , and gives, by (47) and (48),

$$\frac{G}{F} = \frac{\frac{\zeta_{l}}{\zeta} - \frac{l_{l}}{l}}{\frac{\zeta_{l}}{\zeta} + \frac{l_{l}}{l}} = \frac{\frac{\sin^{2} i}{\sin^{2} i_{l}} - \frac{\cot i_{l}}{\cot i}}{\frac{\sin^{2} i}{\sin^{2} i_{l}} + \frac{\cot i_{l}}{\cot i}} = \frac{\tan (i - i_{l})}{\tan (i + i_{l})} \quad . \quad (64),$$

which is Fresnel's "tangent-formula."

XLVII. Van't Hoff's Hypothesis and the Constitution of Benzene. By J. E. Marsh, B.A.\*

THE hypothesis of Van't Hoff is based on the fundamental principle that the four valencies of the carbon atom are directed from the centre of a regular tetrahedron towards the angles. Without entering into any detailed explanation, I may be allowed briefly to notice that from this fundamental principle follows the isomerism of bodies containing a carbon atom combined with four different groups (called an asymmetric carbon atom), and this isomerism is found actually to exist, and is characterized by possession by the two isomeric compounds of enantiomorphous crystalline form and opposite rotatory power. The two compounds are in fact represented by formulæ in space related to one another as the object to its image, the object being different from and not superposable on its image, though the dimensions of both are the same.

Further, there follows from the fundamental principle that there is an isomerism of a different nature from the preceding among bodies which contain more than one asymmetric carbon atom, an isomerism not characterized by rotatory power, an example of which is found in the case of racemic

and inactive mesotartaric acids.

Again, there follows an isomerism in the case of two doubly linked carbon atoms, each combined with two different groups, an isomerism called "geometrical isomerism," and "alloisomerism," of which a familiar example is to be found in the case of maleic and fumaric acids; and all the above classes of isomerism, well established by numerous examples, are inexplicable by the old structural formulæ as expressed on a plane.

$$CH_{2}$$
 $H_{2}C$ 
 $CH_{2}$ 
 $H_{2}C$ 
 $CHC_{3}H_{7}$ 
 $NH$ 

Fig. 1 (Conine).

There is further another class of isomerisms, not of particularly recent observation, but one which I wish to deal with in more detail, as it appears to entail a slight modification or rather extension of the original conception of the theory.

\* Communicated by the Author, having been read before the British Association Meeting at Bath, 1888.

I refer to the case where the asymmetric carbon atom forms one of a closed chain or ring of atoms. As examples may be mentioned, conine,  $\alpha$  pipecoline,  $\alpha$  ethyl piperidine, camphor, and the terpenes.

Dealing with the whole class preferably by an example, let

us consider the case of conine (fig. 1).

Now, if we replace the carbon atom to which the propyl group is attached by its image, effected by exchange of place of two of the groups attached to it, we obtain a formula related to the original formula also as the image to its object, and not superposable on it. Conine is of course active, and yet this carbon atom is not attached to four different groups, for it is attached by two bonds to the same group, namely to the whole group of atoms in the molecule. Hence we are led to this extension of the original conception, namely, that the asymmetric carbon atom is not only one to which four different groups are attached, but more generally one which when replaced by its image in the formula of a compound gives rise to the formula of a different compound. The latter in fact includes the former as a particular case.

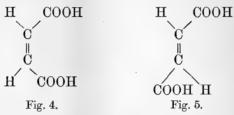
There is, I think, a further extension of the conception of the asymmetric carbon atom necessary, an extension by which is excluded in certain cases the possibility of the existence of active bodies in spite of the presence of asymmetric carbon. Dealing with this case also preferably by an example, let us consider the case of the compound hexahydroterephthalic acid (v. Baeyer, Ann. ccxlv. p. 128). This compound presents a peculiar case of geometrical isomerism (figs. 2 and 3)

analogous to fumaric and maleic acids.

The two carbon atoms to which the carboxyl groups are attached are in fact doubly linked, not directly as in the case of maleic and fumaric acids, but indirectly through the intervention of other groups.

Now von Baeyer has pointed out that the carbon atoms in question are asymmetric; and it will be clear that if one of them, in fig. 2 for example, is replaced by its image the formula so obtained is not identical with the original formula. It is not, however, related to the original compound also as image to object, but is in fact that of the other geometrical isomer (fig. 3).

Again, if we consider the case of two carbon atoms doubly linked and united each to two different groups besides, the case for example of maleic and fumaric acids (figs. 4 and 5),



we find that if one of the doubly linked carbon atoms is replaced by its image, it gives rise to the other geometrical isomer. The carbon atoms in question are in fact asymmetric, and there is here no question of optical activity. Maleic and fumaric acids are in fact devoid of rotatory power. Hence we require an extension of the original conception to include cases where the asymmetric carbon atom, in virtue of its asymmetry, gives rise not to optically different or opposite isomers, but to geometrically different or opposite isomers; and I think the modification and extension of the original conception, as elucidated in the preceding pages, may fairly be expressed in the conclusions following.

1. If in the formula of a compound a carbon atom, being replaced by its image, gives rise to the formula of a compound different from the original one, such carbon atom will

be asymmetric.

2. If the asymmetric carbon atom is replaced by its image, and if the formula so obtained is related to the original formula also as image to object, the two isomers will be optically opposite, *i. e.* will have equal and opposite rotatory power.

3. If the asymmetric carbon atom is replaced by its image, and the formula so obtained is not related to the original formula also as image to object, the isomers will be geometrically opposite and not necessarily possessed of rotatory power, the rotatory power being absent from all isomers in the case where the image of each of the geometrical isomers is identical with the object.

From this it will appear that mesotartaric acid for example is to be regarded as a geometrical isomer of dextro- and lævotartaric acids, which two are optical isomers of one another. Maleic and fumaric acids, again, are geometrical isomers of which optical isomers are wanting. This isomerism, whether optical or geometrical, is due to the presence of carbon atoms, whose images are different from the original atoms, carbon atoms in short which are asymmetric.

I come now to the consideration of the constitution of benzene and to the expression of its constitution on the assumption of the tetrahedric carbon atom.

Former attempts in this direction have led rather to a preference being assigned to the symbol of Prof. Kekulé, of alternate double and single linking, and this symbol can readily be represented on the tetrahedric formation (fig. 6).

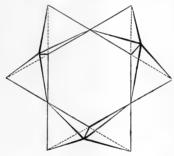


Fig. 6.

Note.—In the figures of the models (6, 8, 9, 11) the carbon atoms are represented by the tetrahedrons, the hydrogen atoms are not given but are supposed to occupy the free angles of the tetrahedrons.

Such a formula perhaps brings into prominence a grave objection to Kekulé's symbol as to the positions 1:2 and 1:6 being identical, and shows the difficulty of assuming the double and single linkings to change places with one another.

But the symbol of Kekulé, and with it its geometric interpretation, may be said now almost to have received their death-blow at the hands of Prof. v. Baeyer. In his work on the hydroterephthalic acids (Ann. ccxlv. p. 103) he shows that these acids act as fatty compounds, the hexa acid as a saturated, the tetra and dihydro acids as unsaturated fatty compounds, and that, indeed, in the latter two acids it is possible to determine between what carbon atoms the double linkings lie. But when we come to terephthalic acid itself

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the case is different, we have no longer a simple repetition of the dehydrogenizing process. It is not a mere change from a single to a double linking which gives us terephthalic from dihydroterephthalic acid. The change is much more profound. Hence we are unable to assert that in terephthalic acid or in benzene we have carbon atoms united alternately by double and single linkings.

The constitution of benzene, to which v. Baeyer is led, is essentially the same as that previously proposed by Prof. Armstrong (this Journal, 1887, vol. xxiii. p. 108), namely, that the six carbon atoms are singly linked, and that the six free affinities react each upon all the rest, and are directed

\*towards the centre of the system.

Now, can we interpret such a constitution as this on the hypothesis of the tetrahedric grouping? Or, to put it in a more concrete form, can we represent the six carbon atoms of benzene and their mode of union with one another by means of regular tetrahedrons which shall represent the carbon atoms and have their affinities situated at the angles? There can in fact be constructed eight different geometrical formulæ for benzene satisfying the above conditions, of which two are represented.

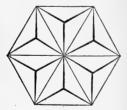


Fig. 8.

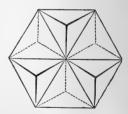


Fig. 9.

The others being constructed by supposing the carbon atoms to occupy different positions with regard to the plane passing through their points of union: thus 5 on one side of the plane and 1 on the other, or 4 on one and 2 on the other, and also by different orientation. Now we know no isomers of benzene, and it may be that benzene fulfils the conditions of all the eight formulæ or of only one of them. Let us consider the two given as being perhaps the most probable. Of these, the first

(fig. 8) is practically identical with that adopted by von Baeyer in the paper mentioned, though he does not put it into such a definite form. In this formula all the hydrogen atoms are on the same side of the ring plane, while in the formula (fig. 9) the hydrogen atoms are alternately on different sides of this plane. Von Baever gives sufficient ground for the adoption of the first formula, and it is also clear that this formula better accounts for the di- and tetra-additive compounds of benzene. The other formula (fig. 9), however, suggests a reason for the well-known association para and ortho, and the isolation of the meta disubstitution derivatives, from the fact that the atoms in the ortho and para positions are on different sides of the ring-plane, and those in the meta position on the same side. It will be noticed that centres of the carbon atoms (fig. 9) occupy the angles of an octahedron (see Thomsen, Ber. xix. p. 2944) resembling Thomsen's octahedral formula in the fact that the diagonal bonds (being formed of the six affinities directed towards the centre of the system) are different in nature from the peripheral, which connect only individual carbon atoms, but differing from his conception in the fact that these diagonal bonds and not the peripheral are broken to give the hexamethylene nucleus.

It is perhaps most probable that of the two formulæ the one which represents all the hydrogen atoms on the same side of the ring-plane is the one most in accordance with facts.

Now it will be noticed that in these formulæ all the carbon atoms are asymmetric, and if replaced respectively by their images give rise to the formulæ of geometrical isomers. The bodies so obtained are in fact the eight theoretically possible isomeric benzenes, previously mentioned, obtained by successive replacements of one or more of the six carbon atoms by their images, but we have no evidence as to the existence of any such isomers.

There is an objection which attaches itself to these formulæ, and it is one which appears also, from the statement of Hermann (Ber. xxi. p. 1958), to attach itself to every benzene formula except when all the 12 atoms lie in one plane. It is an objection also to the old prism formula, though I am not

aware that it has been brought forward before.

The objection is this, that disubstituted derivatives of benzene which contain two different substituting groups in the ortho and meta positions, are each capable of representation respectively by two formulæ, of which one is the non-superposable image of the other, leading us to the prediction of an isomerism which from analogy we should expect to be characterized by rotatory power, while the properties of the

isomers in general would be identical. Such isomers in the case of benzene derivatives we are not acquainted with; we might have expected, for instance, that salicylic aldehyd, which contains two different substituting groups in the ortho position, and which is also a body occurring in nature, would have possessed rotatory power, and would have had an isomer

of equal but opposite rotatory power.

But it may be that the isomerism in question, not being due to an asymmetric carbon atom, is one which is not characterized by the same properties as those whose isomerism is due to such an atom, and that the two isomers have always been obtained as a mixture in equivalent proportions that we know no means of separating them, that if separated they possess identical properties in most respects, and that we know of no special property by which they may be distinguished.

In conclusion, it remains to be noticed that the constitution of benzene, as established by von Baeyer, or as I have endeavoured to modify it, is one which is peculiar to benzene and its substitution derivatives; it disappears in the case of additive derivatives when the ordinary single and double linkings take its place; a saturation of any two carbon atoms, as in dihydroterephthalic acid, or as in quinone, at once annihilates the peculiar character of the benzene ring.

Hence it will be obvious that naphthalene and phenanthrene must be excluded from the category of benzene derivatives. The constitution of naphthalene, as composed of two benzene nuclei having two carbon atoms in common, breaks down because it is impossible for two benzene nuclei to have any of their carbon atoms in common. The free affinities cannot in fact be directed at the same time towards the centres of two hexagons.

Thus, without altering the original formula of naphthalene, we must alter our conception of the body and regard it not as a benzene derivative but as analogous to the unsaturated fatty compounds with six single and five double linkings (figs. 10 and 11).

And if we examine the properties of naphthalene we do not find that it sustains the character of a benzene derivative. The production of phthalic acid from it is not in favour of such a view any more than the production of terephthalic acid from succinosuccinic ether is in favour of this latter body containing a benzene nucleus.

Against the notion that naphthalene consists of two benzene nuclei we have the fact of the comparatively easy oxidation of one of the nuclei giving phthalic acid or naphthaquinone, contrasted with the difficulty of so oxidizing benzene and

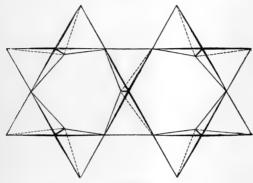


Fig. 11.

compared with the easy oxidation of anthracene, where there is no supposition of the benzene nature of the groups oxidized. Again, we have the easy formation of addition products, such as tetrahydronaphthalene, contrasted with the difficulty of so reducing benzene.

And these reactions receive a natural explanation when naphthalene is considered as an unsaturated fatty compound. For it will be noticed that only one of the hexagons of the naphthalene formula is attacked; the unattacked hexagon may then be regarded as passing into the peculiar benzene condition which renders it less susceptible of further attack.

Thus we have phthalic acid:

Naphthaguinone: -

The oxidation not further affecting the second ring. Tetrahydronaphthalene:-

The addition not going further than to the extent of 4 univalent atoms.

I have adopted in this paper a method of treatment of the carbon atom in space somewhat different from the original conception of it as an atom situated at the centre and having its affinities directed towards the angles of a regular tetrahedron, in that I have treated it as itself representable by a regular tetrahedron having its four affinities acting at the angles. It is, I think, a natural and perfectly legitimate method of treatment, and is in full accordance with Wislicenus' conception, when he states (Ber. xxi. p. 584), "Ich halte es nicht für unmöglich dass das Kohlenstoffatom ein Gebilde sei welche in seiner Gestalt einem regulären Tetraëder mehr oder weniger vielleicht recht sehr ähnelt."

XLVIII. On Electromagnetic Waves, especially in relation to the Vorticity of the Impressed Forces; and the Forced Vibrations of Electromagnetic Systems. By OLIVER HEAVISIDE.

[Continued from p. 382.]

CYLINDRICAL ELECTROMAGNETIC WAVES.

N concluding this paper I propose to give some cases of cylindrical waves. They are selected with a view to the avoidance of mere mathematical developments and unin-

telligible solutions, which may be multiplied to any extent; and for the illustration of peculiarities of a striking character. The case of vibratory impressed E.M.F. in a thin tube is very rich in this respect, as will be seen later. At present I may remark that the results of this paper have little application in telegraphy or telephony, when we are only concerned with long waves. Short waves are, or may be, now in question, demanding a somewhat different treatment\*. We do, however, have very short waves in the discharge of condensers. and in vacuum-tube experiments, so that we are not so wholly removed from practice as at first appears. But independently of considerations of practical realization, I am strongly of opinion that the study of very unrealizable problems may be of use in forwarding the supply of one of the pressing wants of the present time or near future, a practicable æthermechanically, electromagnetically, and perhaps also gravitationally comprehensive.

50. Mathematical Preliminary.—On account of some peculiarities in Bessel's functions, which require us to change the form of our equations to suit circumstances, it is desirable to exhibit separately the purely mathematical part. This will

also considerably shorten and clarify what follows it.

Let the axis of z be the axis of symmetry, and let r be the distance of any point from it. Either the lines of  $\mathbf{E}$ , electric force, or of  $\mathbf{H}$ , magnetic force, may be circular, centred on the axis. For definiteness, choose  $\mathbf{H}$  here. Then the lines of  $\mathbf{E}$  are either longitudinal, or parallel to the axis; or there is, in addition, a radial component of  $\mathbf{E}$ , parallel to r. Thus the tensor  $\mathbf{H}$  of  $\mathbf{H}$ , and the two components of  $\mathbf{E}$ , say  $\mathbf{E}$  longitudinal and  $\mathbf{F}$  radial, fully specify the field. Their connexions are these special forms of equations (2) and (3):—

<sup>\*</sup> The waves here to be considered are essentially of the same nature as those considered by J. J. Thomson, "On Electrical Oscillations in a Cylindrical Conductor," Proc. Math. Soc. vol. xvii., and in Parts I. and II. of my paper "On the Self-Induction of Wires," Phil. Mag. August and September 1886; viz. a mixture of the plane and cylindrical. But the peculiarities of the telegraphic problem make it practically a case of plane waves as regards the dielectric, and cylindrical in the wires. The "resonance" effects described in my just-mentioned paper arise from the to-and-fro reflexion of the plane waves in the dielectric, moving parallel to the wire. This is also practically true in Prof. Lodge's recent experiments, discharging a Leyden jar into a miniature telegraph-circuit. On the other hand, most of such effects in the present paper depend upon the cylindrical waves in the dielectric; and, in order to allow the dielectric fair play for their development, the contaminating influence of diffusion is done away with by using tubes only when there are conductors. In Hertz's recent experiments the waves are of a very mixed character indeed.

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$$\frac{1}{r}\frac{d}{dr}r\mathbf{H} = (4\pi k + cp)\mathbf{E}, \quad -\frac{d\mathbf{H}}{dz} = (4\pi k + cp)\mathbf{F}, \\
\frac{d\mathbf{E}}{dr} - \frac{d\mathbf{F}}{dz} = \mu p\mathbf{H}, \quad (302)$$

where (and always later) p stands for d/dt. This is in space where neither the impressed electric nor the impressed magnetic force has curl, it being understood that  $\mathbf{E}$  and  $\mathbf{H}$  are the forces of the fluxes, so as to include impressed. From (302) we obtain

$$\begin{cases} \frac{1}{r} \frac{d}{dr} r \frac{d\mathbf{E}}{dr} + \frac{d^{2}\mathbf{E}}{dz^{2}} = (4\pi k + cp)\mu p\mathbf{E}, \\ \frac{d}{dr} \frac{1}{r} \frac{d}{dr} r\mathbf{H} + \frac{d^{2}\mathbf{H}}{dz^{2}} = (4\pi k + cp)\mu p\mathbf{H}, \end{cases}$$
(303)

the characteristics of E and H. Let now

$$q^2 = -s^2 = (4\pi k + cp)\mu p - d^2/dz^2$$
; . . (304)

then the first of (303) becomes the equation of  $J_0(sr)$  and its companion, whilst the second becomes that of  $J_1(sr)$ , and its companion. Thus E is associated with  $J_0$  and H with  $J_1$ , when H is circular; conversely when E is circular.

We have first Fourier's cylinder function

$$J_{0r} = J_0(sr) = 1 - \frac{(sr)^2}{2^2} + \frac{(sr)^4}{2^24^2} - \dots;$$
 (305)

and its companion, which call Go, is

$$G_{0r} = G_0(sr) = (2/\pi) \left[ J_{0r} \log sr + L_{0r} \right],$$
where
$$L_{0r} = \frac{(sr)^2}{2^2} - (1 + \frac{1}{2}) \frac{(sr)^4}{2^2 4^2} + (1 + \frac{1}{2} + \frac{1}{3}) \frac{(sr)^6}{2^2 4^2 6^2} - \dots$$
(306)

The coefficient  $2/\pi$  is introduced to simplify the solutions. The function  $J_1(sr)$  or  $J_{1r}$  is the negative of the first derivative of  $J_{0r}$  with respect to sr. Let  $G_1(sr)$  or  $G_{1r}$  be the function similarly derived from  $G_{0r}$ . The conjugate property, to be repeatedly used, is

$$(J_0G_1-J_1G_0)_r = -2/\pi sr.$$
 (307)

We have also Stokes's formula for  $J_{0r}$ , useful when sr is real and not too small, viz.

$$J_{0r} = (\pi sr)^{-\frac{1}{2}} [R(\cos + \sin) sr + Si(\sin - \cos) sr],$$
 (308)

where R and Si are functions of sr to be presently given. The corresponding formula for  $G_{0r}$  is obtained by changing cos to sin and sin to  $-\cos$  in (308).

Besides these two sets of solutions, we sometimes require to use a third set. A pair of solutions of the  $J_0$  equation is

$$\begin{aligned}
\mathbf{U} &= r^{-\frac{1}{2}} \epsilon^{qr} (\mathbf{R} + \mathbf{S}), \quad \mathbf{W} = r^{-\frac{1}{2}} \epsilon^{-qr} (\mathbf{R} - \mathbf{S}), \\
\text{where} \quad \mathbf{R} &\pm \mathbf{S} = \mathbf{1} \pm \frac{1}{8qr} + \frac{1^2 3^2}{|2(8qr)^2} \pm \frac{1^2 3^2 5^2}{|3(8qr)^3} + \dots
\end{aligned} (309)$$

The last also defines the R and Si in (308). R is real whether  $q^2$  be + or -, whilst S is unreal when  $q^2$  is -, or Si is then

real, s2 being +.

When qr is a + numeric, the solution U is meaningless, as its value is infinity. But in our investigations  $q^2$  is a differential operator, so that the objection to U on that score is groundless. We shall use it to calculate the shape of an inward progressing wave, whilst W goes to find an outward wave. The results are fully convergent within certain limits of r and t. From this alone we see that a comprehensive theory of ordinary linear differential equations is sometimes impossible. They must be generalized into partial differential equations before they can be understood.

The conjugate property of U and W is

$$UW'-U'W = -2q/r$$
, . . . (310)

if the '=d/dr. An important transformation sometimes required is

$$J_{0r} - iG_{0r} = 2iW(2\pi q)^{-\frac{1}{2}}; . . . . . (311)$$

or, which means the same,

$$W = -\left(\frac{2q}{\pi}\right)^{\frac{1}{2}} [J_{0r} \log qr + L_{0r}]. \quad . \quad . \quad (312)$$

When we have obtained the differential equation in any problem, the assumption  $s^2 = a + \text{constant}$  converts it into the solution due to impressed force sinusoidal with respect to t and z; this requires  $d^2/dz^2 = -m^2$ , and  $d^2/dt^2 = -n^2$ , where m and n are positive constants, being  $2\pi$  times the wave-shortness along z and  $2\pi$  times the frequency of

vibration respectively.

After (309) we became less exclusively mathematical. To go further in this direction, and come to electromagnetic waves, observe that we need not concern ourselves at all with F the radial component, in seeking for the proper differential equation connected with a surface of curl of impressed force; it is E and H only that we need consider, as the boundary conditions concern them. The second of (302) derives F from H.

When H is circular, the operator E/H is given by

$$\frac{E}{H} = \frac{s}{4\pi k + cp} \frac{J_{0r} - yG_{0r}}{J_{1r} - yG^{1r}}, \quad . \quad . \quad . \quad (313)$$

where y is undetermined. When E is circular, the operator E/H is given by

 $\frac{E}{H} = \frac{s}{4\pi k + cp} \frac{J_{1r} - yG_{1r}}{J_{0r} - yG_{0r}}. \quad . \quad . \quad . \quad (314)$ 

The use of these operators greatly facilitates and systematizes investigation. The meaning is that (313) or (314)

is the characteristic equation connecting E and H.

51. Longitudinal Impressed E.M.F. in a thin Conducting Tube.—Let an infinitely long thin conducting tube of radius a have conductance K per unit of its surface to longitudinal current, and be bounded by a dielectric on both sides. Strictly speaking the tube should be infinitely thin, in order to obtain instantaneous magnetic penetration, and yet be of finite conductance without possessing infinite conductivity, because that would produce opacity. In this tube let impressed electric force, of intensity e per unit length, act longitudinally, e being any function of t and z. We have to connect e with

E and H internally and externally.

The magnetic force being circular, (313) is the resistance operator required. Within the tube take y=0 if the axis is to be included; else find y by some internal boundary condition. Outside the tube take y=i when the medium is homogeneous and boundless, because that is the only way to prevent waves from coming from infinity; else find y by some outer boundary condition. There is no difficulty in forming the y to suit any number of coaxial cylinders possessing different electrical constants, by the continuity of E and E at each boundary, which equalizes the E/E of its two sides, and so expresses the E of one side in terms of that on the other; but this is useless for our purpose. For the present take E inside, and leave it unstated outside.

At r=a,  $E_a$  has the same value on both sides of the tube, on account of its thinness. In the substance of the tube  $e+E_a$  is the force of the flux. On the other hand H is dis-

continuous at the tube, thus

$$4\pi K(e+E) = H_{(out)} - H_{(in)} = \left(\frac{H}{E} (out) - \frac{H}{E} (in)\right) E_a . (315)$$

In this use (313), and the conjugate property (307), and we at once obtain

$$e = \left[ -1 + \frac{4\pi k + cp}{4\pi Ks} \frac{2y}{\pi sa} \frac{1}{J_{0a}(J_{0a} - yG_{0a})} \right] E_a, \quad (316)$$

from which all the rest follows. Merely remarking concerning k that the realization of (316) when k is finite requires the splitting up of the Bessel functions into real and imaginary parts, that the results are complex, and that there are no striking peculiarities readily deducible; let us take k=0 at once, and keep to non-conducting dielectrics. Then, from (316), follow the equations of E and H, in and out; thus

$$E_{\text{(in)}} \text{ or }_{\text{(out)}} = \frac{J_{or}(J_{0a} - yG_{0a}) \text{ or } J_{0a}(J_{or} - yG_{0r})}{\frac{cp}{4\pi K_8 \pi sa} - J_{0a}(J_{0a} - yG_{0a})} e, \qquad (317)$$

$$\mathbf{H}_{\text{(in)}} \text{ or }_{\text{(out)}} = \frac{cp}{s} \frac{\mathbf{J}_{1r}(\mathbf{J}_{0a} - y\mathbf{G}_{0a}) \text{ or } \mathbf{J}_{0a}(\mathbf{J}_{1r} - y\mathbf{G}_{1r})}{\text{same denominator}}, \text{ . . . (318)}$$

which we can now examine in detail.

52. Vanishing of External Field.  $J_{0a}=0$ .—The very first thing to be observed is that  $J_{0a}=0$  makes E and H and therefore also F vanish outside the tube, and that this property is independent of y, or of the nature of the external medium. We require the impressed force to be sinusoidal or simply periodic with respect to z and t, thus

$$e = e_0 \sin(mz + \alpha) \sin(nt + \beta), \quad . \quad . \quad (319)$$

so that ultimately

$$s^2 = n^2/v^2 - m^2$$
; . . . . . . (320)

and any one of the values of s given by  $J_{0a}=0$  causes the evanescence of the external field. The solutions just given reduce to

$$\begin{aligned}
\mathbf{H} &= -4\pi \mathbf{K} (\mathbf{J}_{1r}/\mathbf{J}_{1a})e \\
\mathbf{E} &= (s/cn)4\pi \mathbf{K} (\mathbf{J}_{0r}/\mathbf{J}_{1a})ie \\
\mathbf{F} &= -(cn)^{-1}4\pi \mathbf{K} (\mathbf{J}_{1r}/\mathbf{J}_{1a})i(de/dz)
\end{aligned}$$
(321)

which are fully realized, because i signifies p/n, or involves merely a time-differentiation performed on the e of (319).

The electrification is solely upon the inner surface of the tube. In its substance H falls from  $-4\pi Ke$  inside to zero outside, and  $E_a$  being zero, the current in the tube is Ke per unit surface.

The independence of y raises suspicion at first that (321) may not represent the state which is tended to after e is started. But since the resistance of the tube itself is sufficient to cause initial irregularities to subside to zero, even were there a perfectly reflecting barrier outside the tube to prevent dissipation of these irregularities in space, there seems no reason to doubt that (321) do represent the state asymptotically tended to. Changing the form of y will only change

the manner of the settling down. We may commence to change the nature of the medium immediately at the outer boundary of the tube. We cannot, however, have those abrupt assumptions of the steady or simply periodic state which characterize spherical waves, owing to the geometrical

conditions of a cylinder.

53. Case of two Coaxial Tubes.—If there be a conducting tube anywhere outside the first tube, there is no current in it, except initially. From this we may conclude that if we transfer the impressed force to the outer tube, there will be no current in the inner. Thus, let there be an outer tube at r=x, of conductance  $K_1$  per unit area, containing the impressed force  $e_1$ . We have

$$E_x = \frac{4\pi K_1 e_1}{Y_3 - Y_2 - 4\pi K_1}, \quad (322)$$

where  $Y_3$  and  $Y_2$  are the H/E operators just outside and inside the tube, whilst  $E_x$  is the E at x, on either side of the tube, resulting from  $e_1$ . We have

$$Y_3 = \frac{cp}{s} \frac{J_{1x} - y_1 G_{1x}}{J_{0x} - y_1 G_{0x}}, \quad Y_2 = \frac{cp}{s} \frac{J_{1x} - y G_{1x}}{J_{0x} - y G_{0x}}, \quad . \quad . \quad (323)$$

where  $y_1$  is settled by some external and y by some internal condition. In the present case the inner tube at r=a, if it contains no impressed force, produces the condition

$$Y_2 - Y_1 = 4\pi K$$
 at  $r = a$ , . . . (324)

where  $Y_1$  is the internal H/E operator. Or

 $4\pi K = \frac{cp}{s} \left( \frac{J_{1a} - yG_{1a}}{J_{0a} - yG_{0a}} - \frac{J_{1a}}{J_{0a}} \right),$ 

giving

Now, using (323) in (322) brings it to

$$E_{x} = \frac{(J_{0x} - yG_{0x})(J_{0x} - y_{1}G_{0x})4\pi K_{1}e_{1}}{\frac{cp}{s}(y_{1} - y)\frac{2}{\pi sx} - 4\pi K_{1}(J_{0x} - yG_{0x})(J_{0x} - y_{1}G_{0x})}, \quad (326)$$

in which y is given by (325), and from (326) the whole state due to  $e_1$  follows, as modified by the inner tube.

Now  $J_{0a} = 0$  makes y = 0; this reduces (326) to

$$E_{x} = \frac{J_{0x}(J_{0x} - y_{1}G_{0x})4\pi K_{1}e_{1}}{\frac{cp}{s}y_{1}\frac{2}{\pi sx} - 4\pi K_{1}J_{0x}(J_{0x} - y_{1}G_{0x})}; \quad . \quad (327)$$

and, by comparison with (317) we see that it is now the same as if the inner tube were non-existent. That is, when it is situated at a nodal surface of E due to impressed force in the outer tube, and there is therefore no current in it (except transversely, to which the dissipation of energy is infinitely small), its presence does nothing, or it is perfectly trans-

parent.

It is clearly unnecessary that the external impressed force should be in a tube. Let it only be in tubular layers, without specification of actual distribution or of the nature of the medium, except that it is in layers so that c, k, and  $\mu$  are functions of r only; then if the axial portion be nonconducting dielectric, the  $J_{0r}$  function specifies E and allows there to be nodal surfaces, for instance  $J_{0a}=0$ , where a conducting tube may be placed without disturbing the field. Admitting this property ab initio, we can conversely conclude that e in the tube at r=a will, when  $J_{0a}=0$ , make every external cylindrical surface a nodal surface, and therefore produce no external disturbance at all.

54. Now go back to § 51, equations (317) (318). There are no external nodal surfaces of E in general (exception later). We cannot therefore find a place to put a tube so as not to disturb the existing field due to e in the tube at r=a. But we may now make use of a more general property. To illustrate simply, consider first the electromagnetic theory of induction between linear circuits. Let there be any number of circuits, all containing impressed forces, producing a determinate varying electromagnetic field. In this field put an additional circuit of infinite resistance. The E.M.F. in it, due to the other circuits, will cause no current in it of course, so that no change in the field takes place. Now, lastly, close the circuit or make its resistance finite, and simultaneously put in it impressed force which is at every moment the negative of the E.M.F. due to the other circuits. Since no current is produced there will still be no change, or everything will go on as if the additional circuit were nonexistent.

Applying this to our tubes, we may easily verify by the previous equations that when there are two coaxial tubes, both containing impressed forces, we can reduce the resultant electromagnetic field everywhere to that due to the impressed force in one tube, provided we suitably choose the impressed

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force in the second to be the negative of the electric force of field due to e in the first tube when the second is nonexistent. That is, we virtually abolish the conductance of

the second tube and make it perfectly transparent.

55. Perfectly Reflecting Barrier. Its effects. Vanishina of Conduction Current.—To produce nodal surfaces of E outside the tube containing the vibrating impressed force, we require an external barrier, which shall prevent the passage of energy or its absorption, by wholly reflecting all disturbances which reach it. Thus, let there be a perfect conductor at r=x. This makes E=0 there. This requires that the y in (317), (318) shall have the value  $J_{0x}/G_{0x}$ , whereas without any bound to the dielectric it would be i. We can now choose m and n so as to make  $J_{0x} = 0$ . This reduces those equations to

(in and out)
$$E = -\frac{J_{0r}}{J_{0a}}e; \quad F = -\frac{1}{s}\frac{J_{1r}}{J_{0a}}e;$$

$$H = -\frac{1}{s}\frac{J_{1r}}{J_{0a}}cpe.$$
(328)

This solution is now the same inside and outside the tube containing the impressed force, and there is no current in

the tube, that is, no longitudinal current.

To understand this case, take away the impressed force and the tube. Then (328) represents a conservative system in stationary vibration. Now, by the preceding, we may introduce the tube at a nodal surface of E without disturbing matters, provided there be no impressed force in the tube. But if we introduce the tube anywhere else, where E is not zero, we require, by the preceding, an impressed force which is at every moment the negative of the undisturbed force of the field, in order that no change shall occur. Now this is precisely what the solution (328) represents, e in the tube being cancelled by the force of the field, so that there is no conduction-current. The remarkable thing is that it is the impressed force in the tube itself that sets up the vibrating field, and gradually ceases to work, so that in the end it and the tube may be removed without altering the field. perfect conductor as reflector is required is a detail of no moment in its theoretical aspect.

Shifting the tube, with a finite impressed force in it. towards a nodal suface of E, sends up the amplitude of the

vibrations to any extent.

56. K=0 and  $K=\infty$ .—If the tube have no conductance. e produces no effect. This is because the two surfaces of

curl of e are infinitely close together, and therefore cancel, not having any conductance between them to produce a dis-

continuity in the magnetic force.

But if the tube have infinite conductance, we produce complete independence between the internal and external fields, except in the quite unessential particular that the two surfaces of curl e are of opposite kind and time together. Equations (317), (318) reduce to

(in) 
$$E = -\frac{J_{0r}}{J_{1a}^{-2}}e$$
,  $F = -\frac{1}{s}\frac{J_{1r}}{J_{0a}}e$ ,  $H = -\frac{1}{s}\frac{J_{1r}}{J_{0a}}cpe$ . (329)

$$\begin{cases}
E = -\frac{J_{0r} - y G_{0r}}{J_{0a} - y G_{0a}} e, \quad F = \frac{1}{s} \frac{J_{1r} - y G_{1r}}{J_{0a} - y G_{0a}}, \\
H = -\frac{1}{s} \frac{J_{1r} - y G_{1r}}{J_{0a} - y G_{0a}} epe.
\end{cases} (330)$$

Observe that (329) is the same as (328). The external solution (330) requires y to be stated. When y=i, for a boundless dielectric, the realization is immediate.

57. s=0. Vanishing of E all over, and of F and H also internally.—This is a singularity of quite a different kind. When n=mv, we make s=0. Of course there is just one solution with a given wave-length along z: a great frequency with small wave-length, and conversely.

E vanishes all over, that is both inside and outside the tube containing e, provided s/y is zero. The internal H and therefore also F vanish. Thus within the tube is no dis-

turbance, and outside, (317) (318) reduce to

(out) 
$$H = \frac{a}{r} 4\pi Ke$$
,  $F = \frac{1}{cn} \frac{a}{r} 4\pi Ki \frac{de}{dz}$ . . . . (331)

Observe that H and F do not fluctuate or alternate along r, but that H has the same distribution (out from the tube) as if e were steady and did not vary along z.

A special case is m=0. Then also n=0, or e is steady and independent of z. F vanishes, and the first of (331) ex-

presses the steady state.

Without this restriction, the current in the tube is Ke per unit surface, owing to the vanishing of the opposing longitudinal E of the field. This property was, by inadvertence, attributed by me in a former paper \* to a wire instead of a

<sup>\* &</sup>quot;On Resistance and Conductance Operators," Phil. Mag. Dec. 1887, p. 492, Ex. j.

tube. The wave-length must be great in order to render it applicable to a wire, because instantaneous penetration is assumed.

I mentioned that s/y must vanish. This occurs when y=i, or the external dielectric is boundless. But it also occurs when E=0 at r=x, produced by a perfectly conductive screen. This is plainly allowable because it does not interfere with the E=0 all over property. What the screen does is simply to terminate the field abruptly. Of course it is electrified.

58. s=0 and  $H_x=0$ .—But with other boundary conditions, we do not have the solutions (331). Thus, let  $H_x=0$ , instead of  $E_x=0$ . This makes  $y=J_{1x}/G_{1x}$  in (317), (318). There are at least two ways (theoretical) of producing this boundary condition. First, there may be at r=x a screen made of a perfect magnetic conductor  $(g=\infty)$ . Or, secondly, the whole medium beyond r=x may be infinitely elastive and resistive (c=0, k=0) to an infinite distance.

Now choose s=0 in addition and reduce (317), (318).

The results are

$$\mathbf{E} = -\frac{e}{1 + \frac{1}{2}x^2cp/4\pi\mathbf{K}a}; \quad \mathbf{F} = -\frac{1}{cp}\frac{d\mathbf{H}}{dz},$$
(in) or (out)  $\mathbf{H} = -\frac{cpe}{1 + \frac{1}{2}x^2cp/4\pi\mathbf{K}a}\left(\frac{r}{2}\text{ or }\frac{r}{2} - \frac{x^2}{2r}\right),$  (332)

which are at once realized by removing p from the denominator to the numerator.

Although E is not now zero, it is independent of r, only

varying with t and z.

When  $s^2$  is negative, or n < m/v, the solutions (317), (318) require transforming in part because some of the Bessel functions are unreal. Use (312), because q is now real. There are no alternations in E or H along r. They only commence when n > mv.

59. Separate actions of the two surfaces of curl e.—Since all the fluxes depend solely upon the curl of e and not upon its distribution, and there are two surfaces of curl e in the tube problem, their actions, which are independent, may be separately calculated. The inner surface may arise from e in the — direction in the inner dielectric, or by the same in the + direction in the tube and beyond it. The outer may be due to e in the — direction beyond the tube, or in the + direction in the tube and inner dielectric.

We shall easily find that the inner surface of curl of e, say

of surface density  $f_1$ , produces

(in) 
$$E = J_{0r} \frac{(J_{1a} - yG_{1a}) - (J_{0a} - yG_{0a}) 4\pi Ks/cp}{2y/\pi sa - J_{0a}(J_{0a} - yG_{0a}) 4\pi Ks/cp} f_1$$
  
(out)  $E = \frac{J_{1a}(J_{0r} - yG_{0r})}{\text{same denominator}} f_1$  (333)

from which H may be got by the E/H operator.

The external sheet, say  $f_2$ , produces

(in) 
$$\mathbf{E} = \frac{\mathbf{J}_{0r}(\mathbf{J}_{1a} - y\mathbf{G}_{1a})}{\cdot \cdot \cdot \cdot \cdot \cdot} f_2,$$
  
(out)  $\mathbf{E} = (\mathbf{J}_{0r} - y\mathbf{G}_{0r}) \frac{\mathbf{J}_{1a} + \mathbf{J}_{0a}4\pi\mathbf{K}s/cp}{\cdot \cdot \cdot \cdot \cdot \cdot \cdot} f_2,$   
we approximate denominators are as in the first of (333)

where the unwritten denominators are as in the first of (333). Observe that when  $J_{1a}=0$ ,  $f_1$  produces no external field (in tube or beyond it). It is then only  $f_2$  that operates in the tube and beyond.

Now take  $f_2 = e$  and  $f_1 = -e$  in (333) and (334) and add the results. We then obtain (317), (318); and it is now  $J_{0a} = 0$ that makes the external field vanish, instead of J<sub>1a</sub>=0 when

 $f_1$  alone is operative.

Having treated this problem of a tube in some detail, the other examples may be very briefly considered, although they

too admit of numerous singularities.

60. Circular Impressed Force in Conducting-tube.—The tube being as before, let the impressed force e (per unit length) act circularly in it instead of longitudinally, and let e be a function of t only, so that we have an inner and an outer cylindrical surface of longitudinally directed curl of e. evidently longitudinal and E circular, so that we now require to use the (314) operator.

At the tube  $E_a$  is continuous, this being the tensor of the force of the flux on either side, and H is discontinuous thus,

$$H_{(in)}-H_{(out)}=4\pi K(e+E_a)$$
,

or

$$e = -\left\{1 + \frac{1}{4\pi K} \left(\frac{H}{E} \text{ (out)} - \frac{H}{E} \text{ (in)}\right)\right\} E_a.$$
 (335)

Substituting the (314) operator, with y=0 inside, and y undetermined outside, and using the conjugate property (307), we obtain

$$H_{(in)} \text{ or } _{(out)} = -i \frac{(J_{1a} - yG_{1a})J_{0r} \text{ or } J_{1a}(J_{0r} - yG_{0r})}{\mu v J_{1a}(J_{1a} - yG_{1a}) + \frac{y}{4\pi K} \frac{2v}{\pi ap}} e, (336)$$

$$E_{(in)} \text{ or }_{(out)} = -\mu v \frac{(J_{1a} - yG_{1a})J_{1r} \text{ or } J_{1a}(J_{1r} - yG_{1r})}{\text{same denominator}} e. (337)$$

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When e is simply periodic,  $J_{1a}=0$  makes the external E and H vanish independent of the nature of y. The complete solution is then

$$H_{(in)} = 4\pi K \frac{J_{0r}}{J_{0a}} e, \quad E_{(in)} = -4\pi K \mu v \frac{J_{1r}}{J_{0a}} i e.$$
 (338)

The conduction-current in the tube is  $K_{\ell}$  per unit area of surface.

To make the conduction-current vanish by balancing the impressed force against the electric force of the field that it sets up, put an infinitely conducting screen at r=x outside the tube and choose the frequency to make  $J_{1x}=0$ , since we now have  $y=J_{1x}/G_{1x}$ . We shall then have the same solution inside and outside, viz.

$$H = -\frac{1}{\mu v} \frac{J_{0r}}{J_{1a}} i e, \quad E = -\frac{J_{1r}}{J_{1a}} e; \quad . \quad . \quad (339)$$

so that at the tube itself E = -e. This case may be interpreted as in § 55, the tube being at a nodal surface of E.

A special case of (338) is when n=0, or **e** is steady. Then there is merely the longitudinal **H** inside the tube, given by

$$H = 4\pi Ke$$
.

61. Cylinder of longitudinal curl of e in a Dielectric.—
In a nonconductive dielectric let the impressed electric force be such that its curl is confined to a cylinder of radius a, in which it is uniformly distributed, and is longitudinal. Let f be the tensor of curl e, and let it be a function of t only. Since E is circular and H longitudinal, we have (314) as operator, in which k is to be zero. This is outside the cylinder. Inside, on the other hand, on account of the existence of curl e, the equation corresponding to (314) is

$$\frac{E}{H - f/\mu p} = \frac{s}{cp} \frac{J_{1r}}{J_{0r}}.$$
 (340)

At the boundary r=a both E and H are continuous; so, by taking r=a in (340) and in the corresponding (314) with k=0, and eliminating  $E_a$  or  $H_a$  between them, we obtain the equation of the other. We obtain

(out) 
$$\left\{ \begin{array}{l} \mathbf{E} = \frac{1}{2}\pi a y^{-1} \mathbf{J}_{1a} (\mathbf{J}_{1r} - y \mathbf{G}_{1r}) f, \\ \mathbf{H} = \frac{1}{2}\pi a y^{-1} \mathbf{J}_{1a} (\mathbf{J}_{0r} - y \mathbf{G}_{0r}) (\mu v)^{-1} i f, \end{array} \right\} ... (341)$$

in which y, as usual, is to be fixed by an external boundary condition, or, if the medium be boundless, y=i

We see at once that  $J_{1a}=0$ , with f simply periodic, makes the external fluxes vanish. We should not now say that it

makes the external field vanish, though the statement is true as regards H, because the electric force of the field does not vanish; it cancels the impressed force, so that there is no flux. This property is apparently independent of y. But, since there is no resistance concerned, except such as may be expressed in y, it is clear that (341) sinusoidally realized cannot represent the state which is tended to after starting f, unless there be either no barrier, so that initial disturbances can escape, or else there be resistance somewhere, to be embodied in y, so that they can be absorbed, though only through an infinite series of passages between the boundary and the axis of the initial wave and its consequences.

Thus, with a conservative barrier producing E=0 at r=x, and  $y = J_{1x}/G_{1x}$ , there is no escape for the initial effects, which remain in the form of free vibrations, whilst only the forced vibrations are got by taking  $s^2 = +$  constant in (341). other part of the solution must be separately calculated.  $J_{1s}=0$ , E and H run up infinitely. If  $J_{1a}=0$  also, the result is ambiguous.

With no barrier at all, or y=i, we have

out 
$$\left\{ \begin{array}{l} \mathbf{E} = -(2a)^{-1} \mathbf{J}_{1a} (\mathbf{G}_{1r} + i \mathbf{J}_{1r}) f_0, \\ \mathbf{H} = (2a\mu v)^{-1} \mathbf{J}_{1a} (\mathbf{J}_{0r} - i \mathbf{G}_{0r}) f_0, \end{array} \right\}$$
 (342)

which are fully realized. Here  $f_0 = f\pi a^2$ , which may be called the strength of the filament. We may most simply take the impressed force to be circular, its intensity varying as r within and inversely as r outside the cylinder. Then f=2e/a, if  $e_a$ is the intensity at r=a.

When nr/v is large, (342) becomes, by (308),

(out) 
$$E = \mu v H = \frac{f_0 n}{4v} \left(\frac{2v}{\pi nr}\right)^{\frac{1}{2}} \sin\left(nt - \frac{nr}{v} + \frac{\pi}{4}\right)$$
. (343)

approximately.  $2\pi r$  should be a large multiple, and  $2\pi a$  a

small fraction of the wave-length along r.

62. Filament of curl e. Calculation of Wave. - In the last let  $f_0$  be constant whilst a is made infinitely small. It is then a mere filament of curl of e at the axis that is in operation. We now have, by the second of (342), with  $J_{1a} = \frac{1}{2} na/v$ ,

$$H = -(cp/4)(iJ_{0r} + G_{0r})f_0$$
, . . . (344)

which may be regarded as the simply periodic solution or as the differential equation of H. In the latter case, put in terms of W by (311), then

$$H = (2\mu v)^{-1} (q/2\pi)^{\frac{1}{2}} W f_0;$$
 (345)

448 Mr. O. Heaviside on Electromagnetic Waves, and the or, expanding by (309),

$$\mathbf{H} = \frac{1}{2\mu v} \frac{1}{(2\pi r)^{\frac{1}{2}}} \epsilon^{-qr} \left(1 - \frac{1}{8qr} + \frac{1^2 3^2}{|2(8qr)^2} - \dots\right) q^{\frac{1}{2}} f_0, . (346)$$

in which  $f_0$  may be any function of the time. Let it be zero before and constant after t=0. Then, first,

$$q^{\frac{1}{2}}f_0 = f_0(\pi vt)^{-\frac{1}{2}}$$
. . . . . (347)

Next effect the integrations of this function indicated by the inverse powers of q or p/v, thus

$$f_0\left(1 - \frac{1}{8qr} + \ldots\right)(\pi vt)^{-\frac{1}{2}} = \left(1 - \frac{1}{2}\left(\frac{vt}{2r}\right) + \frac{1 \cdot 3}{2^2|2}\left(\frac{vt}{2r}\right)^2 - \ldots\right)(\pi vt)^{-\frac{1}{2}}$$
$$= (1 + vt/2r)^{-\frac{1}{2}}(\pi vt)^{-\frac{1}{2}} = (2r/\pi)^{\frac{1}{2}}[vt(vt + 2r)]^{-\frac{1}{2}}. \quad (348)$$

Lastly, operating on this by  $e^{-qr}$  turns vt to vt-r, and brings (346) to

$$H = (f_0/2\pi\mu v)(v^2t^2 - r^2)^{-\frac{1}{2}},$$
 (349)

which is ridiculously simple. Let Z be the time-integral of H, then

$$Z = \frac{cf_0}{2\pi} \log \left[ \frac{vt}{r} + \left( \frac{v^2 t^2}{r^2} - 1 \right)^{\frac{1}{2}} \right], \quad . \quad (350)$$

from which we may derive E; thus

curl **Z**=
$$c$$
**E**, or **E**= $-\frac{1}{c}\frac{d\mathbf{Z}}{dr} = \frac{vtf_0}{2\pi r(v^2t^2-r^2)^{\frac{1}{2}}}$ . (351)

The other vector-potential A, such that  $\mathbf{E} = -p\mathbf{A}$  is obviously

$$A = -\frac{1}{2\pi v} \left( \frac{v^2 t^2}{r^2} - 1 \right) . \qquad (352)$$

All these formulæ of course only commence when vt reaches r. The infinite values of E and H at the wave-front arise from the infinite concentration of the curl of e at the axis.

Notice that

everywhere. It follows from this connexion between E and H (or from their full expressions) that

$$cE^2 - \mu H^2 = ce^2 = c(f_0/2\pi r)^2;$$
 . . . (354)

where e denotes the intensity of impressed force at distance r, when it is of the simplest type, above described. That is, the

excess of the electric over the magnetic energy at any point is independent of the time. Both decrease at an equal rate; the magnetic energy to zero, the electric energy to that of

the final steady displacement  $ce/4\pi$ .

The above E and H solutions are fundamental, because all electromagnetic disturbances due to impressed force depend solely upon, and come from, the lines of curl of the impressed force. From them, by integration, we can find the disturbances due to any collection of rectilinear filaments of  $\mathbf{f}$ . Thus, to find the H due to a plane sheet of parallel uniformly distributed filaments, of surface-density f, we have, by (349), at distance a from the plane, on either side,

$$\mathbf{H} = \int \frac{f dy}{2\pi\mu v (v^2 t^2 - a^2 - y^2)^{\frac{1}{2}}} = \frac{f}{2\pi\mu v} \left[ \sin^{-1} \frac{y}{(v^2 t^2 - a^2)^{\frac{1}{2}}} \right],$$

where the limits are  $\pm (v^2t^2-a^2)^{\frac{1}{2}}$ . Therefore

$$H = f/2\mu v$$

after the time t=a/v; before then, H is zero. Similarly, a cylindrical sheet of longitudinal **f** produces

$$\mathbf{H} = \frac{fa}{2\pi\mu v} \int \frac{d\theta}{(v^2 t^2 - b^2)^{\frac{1}{2}}};$$

where b is the distance of the point where H is reckoned from the element  $a d\theta$  of the circular section of the sheet, a being its radius. The limits have to be so chosen as to include all elements of f which have had time to produce any effect at the point in question. When the point is external and vt exceeds a+r the limits are complete, viz. to include the whole circle. The result is then, at distance r from the axis of the cylinder,

$$\mathbf{H} = \frac{fa/\mu v}{(v^2 t^2 - a^2 - r^2)^{\frac{1}{2}}} \left[ 1 + \frac{1 \cdot 3}{2^2 | 2} \frac{x}{2} + \frac{1 \cdot 3 \cdot 5 \cdot 7}{2^4 | 4} \frac{x^2}{2^3} \frac{4 \cdot 3}{1 \cdot 2} + \frac{1 \cdot 3 \cdot 5 \cdot 7 \cdot 9 \cdot 11}{2^6 | 6} \frac{x^3}{2^5} \frac{6 \cdot 5 \cdot 4}{1 \cdot 2 \cdot 3} + \dots \right], \quad (355)$$

where

$$x = (2ar)^{\frac{1}{2}}(v^2t^2 - a^2 - r^2)^{-\frac{1}{2}}.$$

This formula begins to operate when x=1, or vt=a+r. As time goes on, x falls to zero, leaving only the first term.

[To be continued.]

XLIX. Mean Intensity of Magnetization of Soft Iron Bars of Various Lengths in a Uniform Magnetic Field. By A. TANAKADATÉ\*.

[Plates IV. & V.]

THE series of experiments now to be described on the mean intensity of magnetization in soft iron bars of various lengths has been carried out in the Physical Laboratory of Glasgow University, and in accordance with Sir William Thomson's instructions.

The experiments consisted in subjecting the piece of iron to different strengths of magnetizing field, and in measuring the magnetic moment thereby acquired. The amount of residual magnetism was also observed by reducing the field

to zero after each magnetization.

The magnetizing field was obtained as usual by means of an electromagnetic solenoid consisting of fine insulated copper wire, wound upon a brass tube. The length of the wound part of the tube was 11.9 centim., and the total number of turns 13158, so that the magnetic field due to 1 ampere was  $4\pi$   $13158/11.9 \times 10 = 1390$  in C.G.S. units, neglecting the effect due to the broken ends. The current through the solenoid was varied by inserting resistances by steps. Its strength was measured by observing the difference of potentials at the terminals of the solenoid by means of one of Sir William Thomson's graded potential galvanometers †.

The solenoid was laid at right angles to the magnetic meridian, and in the prolongation of the axis of the solenoid was placed a reflecting mirror-magnetometer. Under these circumstances, the deflections of the magnetometer consist of two parts, one due to the solenoid and the other due to the magnetized iron in it. The first of these were taken account of by making a separate observation on the magnetometer deflection without the iron in it, before each experiment.

The iron pieces were cut the required length, and were heated to redness in a gas flame and slowly cooled: the oxide coating formed on the surface was removed by rubbing

\* Communicated by Sir William Thomson, having been read before the British Association at the Bath Meeting, 1888.

<sup>†</sup> The resistance of the solenoid was 406.5 ohms. at  $50^{\circ}$  F., and was assumed to be constant throughout the experiments; as the temperature of the room was never far from that temperature, and the strength of current was never greater than  $_{15}^{\circ}$  ampere, the error arising from the variation of resistance due to that of temperature could not have been anything serious.

with emery paper, except in the experiment represented in

the curve at Pl. IV. fig. 2.

The mean intensity of magnetization was obtained by dividing the magnetic moment of the bar by its volume; the calculation being as follows:—

Let 2l = length of the bar.d = diameter of the bar.

r = distance of the bar's centre from the centre of the magnetometer-needle.

H=the intensity of the horizontal component of the earth's magnetic field (assumed to be 152 C.G.S. unit).

 $\theta$  = deflection of magnetometer.

I = the mean intensity of magnetization.

$$I = \frac{H \tan \theta \ (r^2 - l^2)^2}{l \pi d^2 r}.$$

Tan  $\theta$  was obtained from the observed scale-readings (which are proportional to  $\tan 2\,\theta$ ) by expansion. In the experiment VI., owing to the increased length of the bar, a new solenoid which extended 2.5 centim. beyond the bar toward either way was employed, the constant being 23 C.G.S. units of magnetic field per ampere. This solenoid was placed vertically due west of the magnetometer, the upper end of the iron wire being slightly above the level of the magnetometer. The calculation for the mean intensity in this case was

$$I = \frac{H \tan \theta r^2}{\frac{\pi}{4} d^2 \left\{ 1 - r^3 / (r^2 + l^2)^{\frac{3}{2}} \right\}},$$

where r is the distance of the upper end of the wire from the magnetometer \*.

The results thus arrived at are graphically represented in

figs. 7 to 14 (Pls. IV., V.)

Prof. J. A. Ewing has carried this experiment † from length/diameter = 300 to 50; the 300 one being found to give practically the same results as those obtained with ring-magnets, and the present results might be looked upon as its continuation, had it not been for the difference in the methods employed. Prof. Ewing's method was a ballistic one; consequently it gives the magnetization in the neighbourhood

† Phil. Trans. 1885, Part II.

This experiment VI. is not strictly comparable with the other five, not only on account of the difference in the methods employed, but also on account of the difference in the specimen of iron used.

of the equatorial section of the bar where it will be a maximum, the result being independent of the mode of distribution of magnetism at the broken ends. In the present case, however, the calculation being based upon the supposition of solenoidal distribution (which is far from being true), I might be called the mean intensity of magnetization in the mass of the substance under consideration.

A glance at the diagram shows a rapid fall of mean intensity as the length diminishes. This is no doubt due to the demagnetizing effect of the broken ends, as is noticed in Maxwell's book. It might be interesting here to notice how this demagnetizing force reduces the areas of hysteresis as the ratio length/diameter varies, although with regard to this point I much regret that (except in VI.) I did not complete the whole cycle by subjecting the bars to negative magnetic of the state of the stat

netization. Still, the values of  $\int Id\mathfrak{H}$  obtained from the above

might give some notion with regard to the amount of energy dissipated in carrying different bar-magnets through the cycle of magnetization, § being the intensity of magnetizing field as usual. From considerations of results in which the cycle has been completed, the areas in the above diagrams will be seen to be something like one third of the whole area. The areas computed from the above diagrams are given in the following table and at Pl. IV. fig. 7.

Reference number.	Length.	Diameter.	Length Diameter	$\int_0^{70} I d\mathfrak{H}.$	$3\int_0^{70} \mathbf{I} d\mathfrak{H}.$	$\left   3 \! \int_{0}^{70} \! \mathrm{I} d \mathfrak{H} / \mathrm{J}  ho p.                   $
I.	centim.	centim. 0·152	39.4	ergs. 5560	ergs.	40-74 - 10 - 40
1,	0	0.132	094	3300	16680	4°.74×10-4 C.
II.	5	0.156	32.0	4770	14310	4°.06 ,,
III.	4	0.152	26.3	2964	8892	2°.52 ,,
IV.	3	0.152	19.7	1378	4134	1°·17 ,,
V.	2	0.153	13.1	930	2790	0°.79 "
VI.	33.4	0.115	291.0		18450*	5°.25 "

The last column of the table gives the probable rise of temperature of the iron due to one complete reversal of magnetization, supposing the whole energy dissipated is used in heating the iron.

In connexion with the present result I beg to mention some results of mine which were obtained in 1883 in Japan. The

<sup>\*</sup> This is the whole area of cycle  $\int_{-51}^{+51} Id\mathfrak{p}$ .

experiment was carried out in the Physical Laboratory of the then Tokyo Daigaku. It was very similar to the present one in its nature, conducted, however, in a different way, in so far as the magnetizing field was kept constant while the mass of iron magnetized was increased by steps.

The arrangement of the magnetizing solenoid and the magnetometer was the same as in the present experiment. The dimensions of the solenoid were:—length 9.25 centim.; external diameter 2 centim.; internal diameter 0.86 centim.; number of turns of wire per centimetre 132.6. The length of soft iron wire was 9 centim. and its diameter 1 millim.

In the first experiment the magnetizing field of 46 C.G.S. units was kept constant, and the soft iron wires were put into the solenoid one by one. At first these wires were sucked into the solenoid very vigorously, and the magnetometer readings were very nearly proportional to the number of wires in the solenoid. But when the number of iron wires was about 10, some of the wires began to throw themselves out of the solenoid, and even when pushed in again with a finger would jump out upon its removal.\* They were, however, capable of being kept in their normal position by a careful adjustment. Obviously every one of the wires is under two forces—one, that due to the solenoid, tending to keep the wire in, and the other, due to the magnetism of its fellow wires, tending to push it off: consequently when the latter becomes greater than the former, the wires will be in an unstable state (such a state might be imagined to be taking place between parts of a solid bar). It is interesting to see that, after this event, the magnetometer readings fall rapidly short of being proportional to the number of wires in the solenoid, and after the number was increased to about 25 the magnetometer readings remained practically constant, even if the wires were increased to as many as 41.

Figs. 8 to 14, Pl. V., represent the results of this experiment. Fig. 8 shows the increase of magnetic moment due to the increase of iron wires, and fig. 9 the mean intensity of

magnetization in the whole substance of the iron.

Similar experiments were made for the constant magnetizing fields 50, 11, 5.5, 2.75 C.G.S. units. These are drawn in arbitrary scales for the want of the original notes at the present. By comparing these, however, with the curves for field=46, one can form a fair estimate of what they

<sup>\*</sup> After the number of wires had been increased to 38, they did not jump out even if slightly disturbed from the normal position. But I was unable to tell whether this was a magnetic effect, or simply a mechanical one due to the increase of friction.

would be in C.G.S. units. It thus seems that we may roughly obtain the moments in C.G.S. by multiplying the numbers in the y-ordinate of curves fig. 10 by 6.7, and the mean intensity of magnetization by multiplying the numbers in y-ordinate

of curves fig. 11 by 10.

From the curves (Pl. IV. figs. 1 to 5) I construct the following curves of mean intensity of magnetization as a function of the ratio length/diameter of the bar for different magnetizing fields. From these curves we see that the intensity of magnetization falls very rapidly as the ratio length/diameter diminishes. As this ratio increases the curves will bend toward the x-axis, and will ultimately be parallel to it as long as the magnetization of ring-magnets is finite.

As a means of comparison I construct, from the curves of magnetization with several wires, the diagram (Pl. V. fig. 13) of mean intensity of magnetization as function of length/ $\sqrt{\phantom{a}}$  sectional area  $4/\pi$ , that is, what the ratio length/diameter would become had these wires been moulded into a single cylinder at each step instead of being separate wires side by side, as in the actual case. By comparing this with the curves fig. 12, we see that they both show that for very flat plates the mean intensity will be extremely small; also for the case of separate wires the bend of the curve occurs earlier, *i. e.* for less value of length/diameter.

From the way in which the curves figs. 8 and 10 tend to be asymptotic, it would seem that the induced magnetic moment in a soft iron bar is not increased by increasing its thickness beyond a certain proportion of its length. These curves, however, are in reality obtained from experiments made on a bundle of wires of given length with various thicknesses of the bundle. Thus, there may be material difference between this case and the case in which an actual solid bar of given length is made to vary in its thickness. We have no experiment of this latter case; but if we assume that, when similar bars of the same magnetic substance are placed in uniform magnetic fields of the same intensity. both of them will give the same amount of the mean intensity of magnetization, or, in other words, if we suppose the intensity of magnetization in a uniform magnetic field to be independent of the absolute sizes of the bars, and merely dependent upon the shape and nature of the magnetic substance, then we can trace the increase of magnetic moment due to the increase of section in a bar of given length, from

the data we have in the curves figs. 1 to 5. To do this we have to reduce the bars to some common length and find their several diameters which will make their shapes similar to the original ones. Taking their common length to be 1 cm., and finding the diameters and volumes which each of the bars would come to have, we obtain from the Table given in page 452:—

Reference number.	Reduced diameters.	Reduced volumes.
I. ··	·0253 cm.	'00051 cub. cm.
II.	·0312 ,,	00077 ,, ,,
III.	.0380 "	·00114 " "
IV.	.0507 ,,	.00203 ,, ,,
<b>v</b>	.0765 ,,	00457 ,, ,,

To find, now, the induced magnetic moment due to any field in any of the reduced bars, we have to take the mean intensity of magnetization corresponding to that field from the particular curve which belongs to the original bar; and multiply that intensity by the reduced volume. The diagram (fig. 14) shows the increase of magnetic moment due to the increase of the section of soft iron bars deduced in this way. On the top of the diagram numbers indicating the ratio (diameter/length) are placed for convenience The moment here being given in C.G.S. of reference. units for bars of 1 centim. long, we can find the moment of induced magnetism due to any field for a soft iron bar of any given dimensions, supposing the magnetization to be independent of the absolute size of the bar. For this purpose we have to take the moment corresponding to the particular ratio (diameter/length) of the given bar and the particular field required, and multiply that moment by the cube of the That is to say, within the limits to which the experilength. ments extend.

The curves are similar in character to those obtained with a bundle of wires, only they are not so decidedly asymptotic as the latter. We cannot, however, draw a definite conclusion as to the real difference between the two cases, on account of the difference of the specimens of the wires employed. From both sets of these experiments we see that, after the diameter is about  $\gamma_5$  of the length of the bar, there is not much increase of moment due to the increase of the thickness of the bar; that is, the induced magnetic moment will be practically independent of the mass of the iron. This statement, paradoxical as it sounds, is not much to be wondered at if we consider that, when the bar becomes very thick, the substance of the bar itself will be forming a kind of internal armature to the free ends of the bar. Thus it seems likely, where thick bar magnets are used in practice, that there may be found waste of material of iron, although in many cases different shapes and the presence of external armatures will modify the condition from the case of the experiments described.

Glasgow University, October 10, 1888.

L. On the General Quartine, or the Incriticoid of the Fourth Degree. By the Rev. Robert Harley, M.A., F.R.S.\*

CRITICOIDS are those functions of the coefficients of a / linear differential equation which remain unaltered when the differential equation is transformed by a change of one of the variables, being analogous in this respect to the critical functions or seminvariants of common algebra. We may divide them into two classes, according as the changed variable is the dependent or independent variable. Sir James Cockle, to whom we owe the discovery of these forms †, calls the first class "ordinary," and the second "differential," but in fact both are differential, because both contain differential coefficients. Professor Malet ‡ describes them as Invariants of the first and second class. The functions, however, are not strictly invariants, and the distinction between first and second class hardly seems marked enough. I propose to give the name Decriticoids to those forms which are unaffected by a change of the dependent variable, and the name Incriticoids to those which are unaffected by a change of the independent variable. A decriticoid of the mth degree may be called an m-ide, and an incriticoid of the same degree an m-ine.

\* Communicated by the Author.

† Malet. "On a Class of Invariants," Philosophical Transactions for

1882, Part III. pp. 751-776.

<sup>†</sup> Harley. "Professor Malet's Classes of Invariants identified with Sir James Cockle's Criticoids." Proceedings of the Royal Society for 1884, vol. xxxviii. pp. 45-57.

The object of this paper is not to expound the general theory, or to point out any of its numerous applications, but simply to place on record the explicit form of the quartine or incriticoid of the fourth degree. This form I calculated in February 1885, and communicated at the time to Sir James Cockle; it has not hitherto been printed. Unique in character, its peculiarities deserve attentive study. I hope to consider these in a memoir dealing with the general subject.

Using the quantical notation we may write the linear dif-

ferential equation of the nth order thus—

$$(1, P_1, P_2, \dots P_n) (\frac{d}{dx}, 1)^n y = 0,$$

where  $P_1, P_2, \ldots P_n$  are functions of x. Changing the independent variable, this equation may be transformed into

$$(1, Q_1, Q_2, \ldots Q_n) (\frac{d}{dt}, 1)^n y = 0,$$

where  $Q_1, Q_2, \ldots Q_n$  are functions of t. Denoting differentiations with respect to x by acute, and with respect to t by grave accents, and representing the general quartine by

$$\frac{\phi(\mathbf{Q},\,\mathbf{Q}',\,\mathbf{Q}'',\,\mathbf{Q}''')}{\mathbf{Q}^{\frac{4}{n}}},$$

or its equivalent

$$\frac{\phi(P,\,P',\,P'',\,P''')}{P^{\frac{4}{n}}},$$

the result to which I have been led, omitting here all details of calculation, may be exhibited in the following form, viz.:—

$$\begin{split} \phi(\mathbf{Q},\,\mathbf{Q}',\,\mathbf{Q}'',\,\mathbf{Q}''') &= \mathbf{Q}_1''' + \frac{12}{n-1}\,\mathbf{Q}_1''\,\mathbf{Q}_1 + \frac{4}{n-1}\,(\mathbf{Q}_1')^2 \\ &+ \frac{44}{(n-1)^2}\,\mathbf{Q}_1'\,\mathbf{Q}_1^2 - \frac{5(n-1)}{2(n-4)}\,\mathbf{Q}_4 + 10\,\mathbf{Q}_3\,\mathbf{Q}_1 + \frac{15(n-1)}{2(n-2)}\,\mathbf{Q}_2^2 \\ &- \frac{30(n-2)}{n-1}\,\mathbf{Q}_2\,\mathbf{Q}_1^2 + \frac{15n^3 - 75n^2 + 120n - 38}{(n-1)^3}\,\mathbf{Q}_1^4 \end{split}$$

$$\begin{split} &+\lambda_1 \left\{ Q_2^{\prime\prime} - \frac{2(n-2)}{n-1} \, Q_1^{\prime\prime} \, Q_1 + \frac{10}{n-1} \, Q_2^{\prime} \, Q_1 - \frac{2(n-2)}{n-1} \, (Q_1^{\prime})^2 \right. \\ &- \frac{20(n-2)}{(n-1)^2} \, Q_1^{\prime} \, Q_1^2 - \frac{5(n-2)}{3(n-4)} \, Q_4 + \frac{20(n-2)}{3(n-1)} \, Q_3 \, Q_1 \\ &+ \frac{5n-7}{n-2} \, Q_2^2 - \frac{2(10n-27)}{n-1} \, Q_2 \, Q_1^2 + \frac{(n-2)(10n^2-37n+17)}{(n-1)^3} \, Q_1^4 \right\} \\ &+ \lambda_2 \left\{ Q_3^{\prime} - \frac{3(n-3)}{n-1} \, Q_2^{\prime} \, Q_1 - \frac{n-3}{n-1} \, (Q_1^{\prime})^2 + \frac{(n-3)(3n-8)}{(n-1)^2} \, Q_1^{\prime} \, Q_1^2 \right. \\ &- \frac{5(n-3)}{4(n-4)} \, Q_4 + \frac{5n-9}{n-1} \, Q_3 \, Q_1 + \frac{3(n-3)}{2(n-2)} \, Q_2^2 - \frac{21(n-3)}{2(n-1)} \, Q_2 \, Q_1^2 \\ &+ \frac{(n-3)(21n^2-57n+26)}{4(n-1)^3} \, Q_1^4 \, \right\} \\ &+ \lambda_3 \left\{ \, Q_1^{\prime} \, Q_2 - \frac{n-2}{3(n-1)} \, (Q_1^{\prime})^2 - \frac{(n-2)(3n-1)}{3(n-1)^2} \, Q_1^{\prime} \, Q_1^2 \right. \\ &- \frac{3(n-1)}{4(n-2)} \, Q_2^2 + \frac{3n-1}{2(n-1)} \, Q_2 \, Q_1^2 - \frac{(n-2)(3n-1)^2}{12(n-1)^3} \, Q_1^4 \right\}, \end{split}$$

in which we may assign to the multipliers  $\lambda_1$ ,  $\lambda_2$ ,  $\lambda_3$  any values as constants, or as functions of n only, that we please. I will only add here that the expression into which  $\lambda_3$  is multiplied is to a factor the square of a known form of the quadrine; it is equal in fact to

$$-\frac{n-2}{3(n-1)} \left\{ \ \mathbf{Q_1'} + \frac{1}{2}.\, \frac{3n-1}{n-1}\, \mathbf{Q_1^2} - \frac{3}{2}.\, \frac{n-1}{n-2}\, \mathbf{Q_2} \right\}^2.$$

4 Wellington Square, Oxford, October 10, 1888.

# LI. On a New Barometer, called "the Amphisbana." By T. H. Blakesley,\*

THIS instrument consists of a straight glass tube of uniform internal cross section, closed at one end and open to

\* Communicated by the Physical Society: read June 23, 1888.

the atmosphere at the other. A thread of quicksilver occupies a portion of the tube, the space between the quicksilver and the closed end being occupied by air. A uniformly graduated scale, of any convenient dimensions, but whose zero point is coincident with the closed end, is attached. is no escape for the air contained between the quicksilver and the closed end, this scale serves to determine the volume of this air at any particular moment. The instrument can be suspended vertically with the closed end either upwards or downwards, and in these positions the volumes of the cushioned air, as indicated by the end of the quicksilver thread, can be ascertained. It is clear that when the closed end is upwards this air is subject to a pressure which is the difference between the atmospheric pressure and that due to a column of quicksilver equal in height to the length of the thread. But when the closed end points downwards, the pressure of the cushioned air is the sum of the atmospheric pressure and that due to the length of the thread.

These two observations, then, enable one to find the relation between the atmospheric pressure and that due to the thread

of quicksilver.

Let H be the unknown height of the barometer; l be the length of the thread of quicksilver;

A be the reading of the volume of air enclosed, when the closed end of the tube is upwards;

B be the reading of the volume, when the closed end is downwards.

Then the product of the pressure and volume being the same in the two cases, assuming the temperature constant,

$$(\mathbf{H} - l)\mathbf{A} = (\mathbf{H} + l)\mathbf{B}$$

or

$$H = \frac{A+B}{A-B} l$$
.

Thus the following rule applies:—Divide the sum of the readings by their difference, and multiply by the length of the quicksilver thread.

Since the length of the quicksilver occurs as a factor, it is obviously advantageous that it should be a simple number, as 10 inches. Where centimetres are required, 25 centimetres or 50 centimetres would be convenient quantities.

Here it may be pointed out that the usual correction for temperature may be made once for all, by having the thread

of quicksilver, not exactly 10 inches or 50 centimetres, but such a length as would be 10 inches or 50 centimetres at zero of temperature Centigrade. Then, by taking the simple number for use in the calculation, whatever the real length may, on account of temperature, be, the final result is the reduced barometer.

A convenient length for a portable instrument would be

about 20 inches, with a 10-inch thread of quicksilver.

The diameter of the tube should be small enough to maintain continuity in the quicksilver. 1.2 millim. or one

twentieth of an inch answers very well.

The value of an observation made with this instrument would theoretically not be injured should the quicksilver thread become, through mischance, discontinuous, so long as all the liquid remained in the tube, though it appears that practically the multiplication of ends by subdivision adds a certain amount of friction, and produces sluggishness in the movements of the quicksilver.

In using the instrument for determining mountain elevations, the length of the quicksilver may be left quite undetermined; for the difference of level appears as a function of the *ratio* merely of the two pressures at the points of observa-

tion  $\left(\mathfrak{F}\log\frac{p_1}{p_2}\right)$ , where  $\mathfrak{F}$  is the height of the homogeneous atmosphere. Therefore we can use the ratio of the functions  $\left(\frac{A+B}{A-B}\right)$  of the observations only at the two stations.

In practice the glass tube is sunk into a groove in a light piece of wood provided with two eyes, which serve either for suspension from a nail in a wall, or for attaching a strap or cord for slinging the instrument round the shoulders in climbing. The eye at the open end of the tube will screw in far enough to stop the opening temporarily if that should be desirable; but if care is taken to climb with the closed end downwards, there is small fear of the quicksilver becoming either lost or discontinuous.

The instrument, as made by Messrs. Watson Brothers, of 4 Pall Mall, weighs between 6 and 7 oz.

### LII. Notices respecting New Books.

Recent Text-books of Determinants.

Teoría elemental de las Determinantes, y sus principales aplicaciones al Algebra y la Geometría. Por Félix Amorétti y Carlos M. Morales. (Buenos Ayres: M. Biedma, 1888.)

Elementary Treatise on Determinants. By WILLIAM G. PECK, Ph.D., LL.D. (New York and Chicago: A. S. Barnes & Company, 1887.)

THE first of these books is a fresh and pleasing indication that mathematical studies have taken vigorous root in the University of Buenos Ayres. The change for the better, due in great part to the energy and enthusiasm of Professor Valentin Balbin, deserves cordial recognition in this country, whose financial and trade relations with the Argentine Republic are yearly becoming more and more important. To the supply of text-books Professor Balbin has made important contributions; and the present work, though not bearing his name on the titlepage, claims him as godfather.

As a specimen of printers' handicraft it is very satisfactory; the page is large (larger than that of Salmon's works), the margin is wide, and the type clear and generously spaced. The subject is treated of in three Sections, viz.:—Determinants in General, occupying 71 pages; Determinants of Special Form, occupying 43 pages; and Applications of Determinants, occupying 66 pages. In all three the arrangement is most methodical: definition, theorem, and corollary following in order, with sufficient illustrations and examples interspersed to satisfy any ordinary student.

With the first section very little fault can be found. The historical indications are rather seriously inaccurate—a venial weakness, considering the rarity of such accuracy, and bearing in mind the fact that the authors do not profess to have made any original research on the subject. The reviewer, however, cannot too often point out how misleading it is to say, for example, that Gauss notably advanced the theory of determinants, that the notation

is due to Cauchy, that Leibnitz's notation was

$$\left|\begin{array}{cccc} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{array}\right|$$

or, indeed, that Leibnitz had any notation for determinants at all. These and other such statements the authors should try to verify, *Phil. Mag.* S. 5. Vol. 26. No. 162. *Nov.* 1888. 2 I

in view of a second edition of their book being called for. They will find all the needful passages of Leibnitz, Gauss, Cauchy, &c., carefully reprinted in the 'Proceedings of the Royal Society of

Edinburgh, vol. xiii. pp. 547-590, xiv. pp. 452-518.

The next section or "book" consists of eight chapters—the first dealing with the Adjugate determinant, the second with Symmetric determinants, the third with Skew determinants, the fourth with " determinantes múltiples," the fifth with Circulants, the sixth with Alternants, the seventh with Continuants, and the eighth with Functional determinants. Most of these chapters are very complete and satisfactory, indeed in no foreign text-book is the treatment of special forms more methodical and exhaustive. The only chapter to which objection can be taken is the fourth, but the objectionable part is so fundamental that no mere improvement in the details would do much good. As the term "multiple" determinant is unknown to English-speaking and German mathematicians, the definition with which the chapter opens must be turned to for information. It is as follows: "A determinant which has each of the elements of a single row or of a single column equal to unity is called a multiple determinant." Whatever doubt may exist about the convenience of the new name thus introduced, there can be absolutely none about the inconvenience of the notation ushered in along with it. The determinants

$$\left|\begin{array}{ccc|c} 1 & 1 & 1 \\ a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \end{array}\right|, \qquad \left|\begin{array}{ccc|c} 1 & a_1 & a_2 \\ 1 & b_1 & b_2 \\ 1 & c_1 & c_2 \end{array}\right|,$$

we are told, are denoted by

As an abridgment this notation is clearly not of the slightest consequence; but a much more serious objection is to be found in the fact that it has been used for many years by the best mathematicians in a totally different sense. Still, bad as this may be, it is as nothing compared with the almost incredible blunder of using the notation in the new sense on one page and in another sense on the next. For example, according to the definition we have

whereas we are informed on p. 96 that

Even this is not all. For according to the definition

$$\left\| \begin{array}{cccc} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \end{array} \right\|^{2} \quad \text{and} \quad \left\| \begin{array}{cccc} a_1 & a_2 \\ b_1 & b_2 \\ c_1 & c_2 \end{array} \right\|^{2}$$

are identical, and the latter is shown on page 96 to be equal to zero. Consequently there are to be found in close proximity three mutually incompatible meanings for

$$\left|\begin{array}{ccc} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \end{array}\right|^2.$$

Messrs. Amorétti and Morales are not altogether to blame; they have committed the indiscretion of trusting too faithfully an unreliable European guide. We put it to them, however, to reconsider now and decide whether the "multiple" determinant deserves their support. To us, the "bag and baggage" policy seems the only suitable one for such an usurper.

The Applications which occupy the third "book" are not all of equal importance. The Algebraical and Geometrical are appropriate and well chosen. Of those which are said to concern Trigonometry, the first half is of very doubtful utility, and the second half consists of nothing more than exercises in finding the final expansion of determinants whose elements involve trigonometrical functions.

As we have implied above, the work of the two Argentine civil engineers is on the whole a very creditable performance, and sure to prove valuable to the mathematical students of the Republic. We trust that the demand for it may be such that a revised and

enlarged edition may soon be called for.

The text-book of Professor Peck belongs to a different category, being of an introductory character, and extending only to 48 pages. It is simply and clearly written, giving the fundamental theorems with numerous easy illustrative examples. The term "co-factor" is incorrectly defined; equations that are consistent are said to "consist"; and there are other easily remedied slips or needless peculiarities. To beginners the manual should be very serviceable.

THOMAS MUIR.

Geological and Natural-History Survey of Canada. Annual Report. New Series. Vol. II. (for 1886), 1887. 8vo; pages 1120. With 13 plates of views and sections and 8 maps and long sections. Dawson Brothers: Montreal.

This very thick volume consists of numerous Reports and Maps of investigations and surveys made and carried on under the superintendence of Dr. Alfred R. C. Selwyn, C.M.G., F.R.S., &c., Director of the Canadian Survey. There are thirteen Reports, lettered and paged separately, relating to various portions of the Dominion of Canada, from Nova Scotia to British Columbia, and northward to the Arctic Ocean.

Report "A" (87 pages) is a summary of the operations of the Survey for the year 1886, including work done at the Colonial Exhibition in London; additions to the Library are also enumerated. Report "B" (129 pages, with a map) is on a geological examination of the northern part of Vancouver Island and the adjacent coasts, by Dr. G. M. Dawson. Mr. J. F. Whiteaves describes the fossils; and Prof. J. Macoun catalogues the plants found there. The Meteorology is also noticed. Report "D" (41 pages, with a long section), by Mr. R. G. McConnell, treats of a portion of the Rocky Mountains, chiefly along the line of the Canadian Pacific Railway. Mr. J. B. Tyrrell gives Report "E" (176 pages, with two maps) on a part of Northern Alberta in the North-western Territory, and the western portions of Assiniboia and Saskatchewan. Mr. J. F. Whiteaves describes the fossils in one appendix; and Mr. D. B. Dowling enumerates the Lepidoptera in another; Elevations and Indian names of places are also tabulated.

Report "F" is preliminary (24 pages), by Mr. A. P. Low, on the country between Lake Winnipeg and Hudson Bay. Botanical and Meteorological observations are noted. Dr. R. Bell reports "G" (39 pages) on portions of the At-ta-wa-pish-kat and Albany Rivers (Lonely Lake to James's Bay). Report "J," by Dr. R. W. Ellis (70 pages, with a map), relates to a portion of the Eastern Townships of Quebec, especially to the Counties of Compton. Stanstead, Beauce, Richmond, and Wolfe. Report "M" (39 pages, with two maps) is on the Surface Geology of Northern New Brunswick and South-eastern Quebec, by Mr. R. Chalmers. Report "N" (19 pages, with a map), by Dr. L. W. Bailey and Mr. W. McInnes, treats of portions of the Counties of Victoria, Northumberland, and Restigouche in New Brunswick. Messrs. H. Fletcher and E. R. Faribault in Report "P" (163 pages) deal with the Geology of the Counties of Guysborough, Antigonish, Pictou, Colchester, and Halifax in Nova Scotia. Report "R" (62) pages, with map) consists of Dr. G. M. Dawson's systematized notes accompanying a geological map of the Northern Portion of the Dominion of Canada, East of the Rocky Mountains. These notes are supplementary to the sketch and map of the physical

geography and geology of the Southern part of Canada, published in 1884.

Report "S" (86 pages) is a statistical account, by Mr. E. Coste, of the production, value, exports, and imports of Minerals in Canada during 1886 and previous years. These mineral statistics deal with—antimony, arsenic, asbestus, coal, copper, gold, graphite, gypsum, iron, lithographic stone, manganese, mica, mineral pigments, miscellaneous metals (lead, zinc, tin, mercury), petroleum and naphtha, phosphate of lime, pyrites, salt, silver, and structural Report "T" (42 pages), by Mr. G. Ch. Hoffmann, assisted by Messrs. F. D. Adams and E. B. Kenrick, consists of chemical contributions to the Geology of Canada from the Laboratory of the Survey, and treats of-miscellaneous native minerals (magnetic and non-magnetic platinum, arsenic, cinnabar, apatite, cookeite, uraninite, coracite, uraconite, monazite, and smaltite), natural waters, iron, copper, and manganese ores, gold and silver assavs, and miscellaneous examinations (shell-marl, carbonaceous schist, cement-stone, and a saline deposit).

Topographical, physical, and geological features are of course carefully described wherever the Reports treat of these conditions of country; natural-history occurrences are often noted; and the minerals and other materials of economic use are recorded wherever met with. Frequent and cordial acknowledgments of help and information received from assistants, friends, and casual acquaintances interested in Geology and its branches are freely given; as well as references to previous workers and to books or

memoirs on the subjects under notice.

The 12 pages of Contents and the 29 pages of an elaborate Index add greatly to the value of this handsome and satisfactory book, which will prove to be of great service, not only to the Canadians, but to British and Foreign geologists generally.

## LIII. Intelligence and Miscellaneous Articles.

ACTION OF ELECTRICITY ON THE VESICLES OF CONDENSED WATER. BY J. L. SORET.

IN a dark room a platinum cup containing water is placed on a metal support which is connected with one pole of a Topler's machine. Above this cup a metal point is placed which is connected with the other pole. A Bunsen's burner boils the water in the cup, which is powerfully illuminated by the projection of a large pencil of the electric light. As long as the Topler's machine is not at work the vapour vesicles ascend in the ordinary manner, but as soon as the machine is at work the action of electricity on the vapour is manifested in the most striking manner. For a certain distance from the point to the surface of the water, the clouds collect and whirl along the edge of the cup; under the influence of

the electric light they look to a certain extent like flames. If the point is brought a little nearer the water the vapour disappears completely, although the water commences to boil briskly.

—Archives des Sciences physiques et naturelles, April 1888.

#### ON SOME PHENOMENA OF MIRAGE. BY J. L. SORET.

In travelling by the steamer from Geneva to Evian, between twenty-five minutes past one and twenty minutes to four, on June 4, a very hot day, on which the temperature of the air must have been considerably higher than that of the lake, M. Soret observed the ordinary variations of refraction in these circumstances (fata morgana). The banks, which were really low, appeared as if they terminated in raised beaches; but the phenomenon varied greatly every minute. M. Soret observed also for a few minutes a mirage, described by M. Ch. Dufour (Bulletin de la Soc. Vaudoise des Sc. Nat. 1854, vol. iv. p. 129), between Yvoire and Thonon: looking at a sailing-boat coming near this latter place, the higher sails are seen very white and shining; the lower sails appeared out of shape, elongated vertically, dark, and looking like two confused superposed images.

But the appearance which most struck M. Soret was the following, as he believes it has not yet been observed:—Between Yvoire and Thonon was seen, on the side of the gulf of Anthy, an appearance as of white vapours, the puffs of which were superposed, and were transported to the south-west by the wind. These tongues of vapour, changing every instant, stood out quite bright on a dark The phenomenon lasted rather a long time. M. Soret thinks it due to the variable state of the layers of air, which in certain places presented conditions favourable for the production of mirage, and gave a partial and dark image of the coast between Yvoire and Anthy; further, when the disturbance of the refraction was less pronounced the image of the coast was not produced, and these places appearing white had the appearance of vapours. Speaking generally, the phenomenon should be manifested when we are at the limit at which mirage is produced, and at the same time when the layers of air are not stable.

A fact of some importance is that, at certain moments and for certain favourable positions, a lower and reversed image is seen of objects situate near the surface of the water as during the ordinary mirage, but with less permanency.

On the following days M. Soret often observed the ordinary mirage even when, at any rate on some of those days, the temperature was but little higher than that of the water. Other observers, M. Forel in particular, have sometimes observed the same fact. It is possibly connected with the hygrometric state of the air.—Archives des Sciences physiques et naturelles, September 1888.

# ON THE CHANGES IN THE SPECIFIC HEAT OF LIQUIDS NEAR THE CRITICAL TEMPERATURE. BY P. DE HEEN.

The author used the method of cooling. The steel cooling-vessel is half filled with the liquid in question, and in order to produce a uniform temperature in the whole mass it rotates about a horizontal axis. After being heated it is enclosed in a copper envelope. For ether, amylene, and bromide of ethyle, there was at the critical temperature a sudden diminution in the specific heat.

	Temperature.	Specific heat.
Ether	ſ 18 <b>5</b>	0.547
	⋯ { 180	1.041
Amylene	ſ 175	0.773
	⋯ ( 170	1.500
Bromide of eth	rla ∫ 220	0.233
	<sup>71e.</sup> \ 215	0.852

With aldehyde, which, however, decomposed, there were no ana-

logous phenomena.

The author infers from the behaviour of the former substances that as the critical temperature is reached the gas-forming molecules relinquish their closed curves and describe the rectilinear paths of Clausius.—Bull. Ac. Roy. de Belg. [3] xv. pp. 522-528. Beiblätter der Physik, No. 9, 1888.

#### ELECTROSCOPE FOR PURPOSES OF DEMONSTRATION. BY B. KOLBE.

This electroscope, which has been specially constructed for purposes of demonstration, is visible on a clear ground at a distance of 30 to 50 feet; and gives large deflections, for, when charged, the leaves are almost horizontal. They consist of red silk paper, and are hung in stirrups of fine silvered copper wire at the side of the brass rod, the upper knob of which has a diameter of 2 centim. The length of the leaves is 3.5 to 4 centim., and the breadth about 0.4 centim. The end is provided with a semicircular enlargement which is twisted at right angles, so that it always presents a surface to the observer.

The conducting rod is insulated by a stout ebonite stopper.

It is important to choose a glass which conducts well, in order to get rid of the disturbing influence of the glass sides. Moreover the glass vessel must be so spacious that the leaves, even when charged, are at a distance of 0.5 to 1 centim. from the glass. If the glass is not a good conductor, the vessel should be so wide that the leaves (when horizontal) are at a distance of 2 to 2.5 centim. from the glass.

It appears hitherto to have been usual to take a good insulating

glass for electroscopes, by which these apparatus, especially those with gold and aluminium leaves, often fail in dry air; for such glass acts like a condenser, and only discharges slowly. It is true that good conducting glass is difficult to meet with. Among 184 kinds which I tried I only found 19 which I could use, and only three of these were good: the trouble is, however, rewarded by the never failing working of the electroscope.

If the paper strips are cut off 1 to 2 millim. below the loop, and fine aluminium strips (4 millim. in breadth and 3 to 4 centim. in length, with rounded ends) are fixed on, an electroscope of extraordinary delicacy is obtained. My electroscope of this construction, with condensing-plates of 6.5 centim. diameter, gave a deflection of 55° when the plates were touched with the poles of a bichromate element, while an ordinary aluminium electroscope showed only 15°.

With this aluminium electroscope we can show very distinctly the difference between the arrangement of elements in series and abreast. In the former case, with two Bunsen's elements, the leaves stand almost horizontal.—Zeitschrift für Phys. und Chem. Unterricht, vol. iv. p. 182. Beiblätter der Physik, No. 7, 1888.

#### ON THE VELOCITY OF SOUND IN LIQUIDS. BY T. MARTINI.

The principal results of the investigation are as follows:-

1. Wertheim's hypothesis that a cylindrical column of liquid vibrates like a solid cylinder is untenable; the smallness of Wertheim's numbers arises rather from the influence of the sides of the tubes.

2. The velocity of sound in water increases with the temperature within the ordinary limits of temperature.

3. The velocity of sound in other liquids increases with the

temperature.

4. When gases, liquids, or solids are dissolved in water the velocity of sound increases; this is also the case with other liquids, such as alcohol, which absorbs water, or turpentine in which resins are dissolved.

5. The velocity of sound in saline solutions increases with the quantity of salt dissolved.

6. Solutions of different salts reduced to the same degree of concentration have different velocities.

7. If the same weight of different salts are dissolved in the same weight of water, very different numbers are obtained; these are much greater with salts containing water than with anhydrous salts.

8. If the same weights of anhydrous and of a hydrated salt are dissolved, the velocity of sound in the former is greater than in the latter.—Beiblätter der Physik, No. 8, 1888; from Atti del. R. Ist. Venet. (6) 6.

# LONDON, EDINBURGH, AND DUBLIN

# PHILOSOPHICAL MAGAZINE

AND

# JOURNAL OF SCIENCE.

[FIFTH SERIES.]

### DECEMBER 1888.

LIV. Note on the Conditions of Self-Excitation in a Dynamo Machine. By Silvanus P. Thompson, D.Sc.\*

WHEN about the year 1867 it began to be recognized that a machine constructed on the principle of magnetoelectric induction might be made to excite the magnetism in its own field-magnets, it became usual to explain the phenomenon of self-excitation in language something like the following. There being a small amount of residual magnetism in the core of the stationary electromagnet, very feeble currents will be induced in the secondary or armature-coils when they are set into rotation at any given speed. If these feeble induced currents are now sent round the coil of the fixed electromagnet they will exalt its feeble magnetism, and its inductive action will be stronger; these stronger currents being also sent round the magnet will raise its magnetism still higher, and so by action and reaction the magnetism and the currents grow at a compound-interest rate until the limit fixed by the magnetic saturation of the iron core of the field-magnet is reached.

Long before the true rationale of the limit of self-excitation was assignable, it was known that this method of considering the subject was faulty. Were it true, it would follow that, no matter what the speed of driving, or the resistance in the electric circuit, the magnetism would go on rising until the iron had attained saturation. The facts, on the contrary, are (1) that in self-exciting machines the degree of excitation of the field-magnets depends most emphatically on the speed and

<sup>\*</sup> Communicated by the Physical Society: read May 12, 1888. Phil. Mag. S. 5. Vol. 26. No. 163. Dec. 1888. 2 K

on the resistances of the electric circuit; (2) that for machines which have their exciting coil in series with the armature and main circuit, there is a certain relation between speed and resistance such that they do not excite themselves at all unless the quotient of speed by resistance attains a certain minimum value; (3) that in machines which have their exciting coil connected as a shunt to the main circuit there is again a certain relation between the speed and the electric resistances of the various parts of the circuit, such that with a given speed self-excitation does not take place unless the resistance of the

external circuit exceeds a certain limiting value.

On June 26, 1886, I had the honour of bringing before the Physical Society\* some formulæ relating to the performance of dynamo-electric machines, in which this matter was touched upon, and in which, on the assumption that the law of magnetization might be adequately represented by the Lamont-Frölich formula, expressions were obtained for the relations between speed, magnetization, resistance, and current. As an important conclusion it was shown, always upon the above assumption, that at a given speed of driving and with a given resistance in the electric circuit, the current, of any given series-wound machine, was always less by a certain fixed quantity than that current which would have been produced (at that speed and with the given resistance) had the magnetism been actually at full saturation. This difference between the actual current and the current that there would have been at saturation was a definite number of amperes. and was shown to be that number of amperes which would have been sufficient to produce exactly half-saturation in the given machine. This half-saturating number of amperes I had previously denominated the "Diacritical" current. This proposition having been established, it became obvious that the machine would not excite itself if the speed and resistance were such—the speed so low or the resistance so high—that the current which would have been produced with fieldmagnets independently saturated was less than the diacritical current. Or, if the resistance of the circuit were prescribed, there would obviously be a least-speed of self-excitation.

The assumption in the above investigation of an approximate expression for the law of magnetization necessarily made the argument less satisfactory than would be the case were no such assumption made. In the argument which follows no assumptions are made of an empirical character as to the law of magnetization, absence of secondary phenomena,

<sup>\*</sup> See Phil. Mag. September 1886.

such as electric and magnetic leakage, being the only point assumed.

It is known that the electromotive force of a dynamo may be written

$$\mathbf{E} = n\mathbf{C}\mathbf{N} \; ; \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where E is the electromotive force (in absolute C.G.S. units); n the number of revolutions of the armature per second; C the number of conductors counted round the periphery of the armature, and closed in series; N the whole number of magnetic lines (in C.G.S. units) that traverse the armature.

So, writing  $\Sigma R$  for the sum of the electric resistances (in C.G.S. units) of the circuit in which the electromotive force operates, the current flowing in the circuit may be written as

Again, it is known that the number of magnetic lines in the armature may be calculated by dividing the line-integral of the magnetizing forces by the sum of the magnetic resistances of the "magnetic circuit" of the dynamo. If the machine is joined up with its exciting coil of S convolutions in series with the main circuit, the line-integral of the magnetizing forces will be written as  $4\pi \mathrm{S}i$ . Then, writing  $\Sigma \rho$  as the sum of all the magnetic resistances in the magnetic circuit, we shall have

$$N = \frac{4\pi Si}{\Sigma \rho}. \qquad (3)$$

From (2) we get

and, from (3),

Equating (4) and (5), we have

It will be noticed that this equation contains neither N nor i, and its truth is independent of the relation between i and N. It is true that  $\Sigma \rho$ , which is a factor of the expression on the right-hand side, depends on N, and, in general, increases when N is increased. But the truth of the equation is not affected by the form of the relation between  $\Sigma \rho$  and N; in brief, it is true independently of any assumptions as to the form of the law of magnetization.

On examining the expression on the left hand of the equa-

tion, it will be seen that, for a given dynamo, all its factors, except the speed n, are invariable. Hence the main fact brought out by this equation is that in a series dynamo, driven at constant speed, the product of the magnetic resistance into the electric resistance is a constant. We have here the key to the behaviour of the self-exciting dynamo;—the explanation why it is that the machine, though exciting itself up" at a compound-interest rate," stops short of absolute saturation in the degree to which its magnetization is raised. As the field-magnets get more and more highly magnetized, the magnetic resistance increases. Suppose that such a dynamo, running at a constant speed, works at a certain degree of magnetization when there is a certain resistance in the elec-Suppose that resistance to be now reduced: the tric circuit. current increases; as a result there is higher magnetization, higher electromotive force, and therefore still greater current. To what point will these things go on increasing? Equation (6) gives the answer: until the decrease in the electric resistance is exactly balanced by the increase in the magnetic resistance.

Other phenomena of the action of the dynamo now become more intelligible. As is well known, in ascending magnetizations of iron there is a certain stage at which the magnetic permeability increases, instead of decreasing, with an increase in the magnetization. In a dynamo at this stage of excitation, any increase in the electric resistance, causing a decrease in the current, will also cause an increase in the magnetic resistance; hence this stage of excitation is one of instability. The dynamo is either excited above this stage, or else its excitation falls below this stage—virtually to zero.

The two factors of the product  $\Sigma \rho$ .  $\Sigma R$  are both complex quantities, containing constant as well as variable terms. We

may write  $\Sigma \rho = \alpha + \xi$ .

Here the constant part  $\alpha$  relates to the magnetic resistance of the gap between the armature-core and the polar surface of the field-magnets; which gap, filled partly with copper, partly with air, and partly with insulating materials, possesses, so far as is known, a constant magnetic resistance. The variable part  $\xi$  of the magnetic resistance relates to the iron portions of the magnetic circuit: it is in general the sum of a number of terms such as  $l/\mu A$ , where l is the length, A the sectional area, and  $\mu$  the permeability, for the time being, of the various portions—cores, yoke, &c.

Similarly, we may write

where a stands for the constant part of the electric resistances (armature and main-circuit coils) in the circuit, and x for the variable part; that is to say, the resistance of the external circuit, including under that term not only true ohmic resistances, but also the effects of counter electromotive forces opposed in the path of the current of the machine.

We may now rewrite equation (6) in the following form for the series-wound machine driven at a constant speed:—

$$(\alpha + \xi)(\alpha + x) = \text{constant.} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Now at starting, when as yet the magnetization of the iron is almost zero, the resistance of the iron part of the magnetic circuit is small. Its value is not indeed quite zero, but depends upon the prior history of the iron. It is certainly so small as to be negligible compared with the value of  $\alpha$ . Hence there will be a particular maximum value of x, which we may call  $x_1$ , corresponding to the case when  $\xi=0$ . This maximum value, which will be given by the equation

$$x_1 = \frac{4\pi n \text{CS}}{\alpha} - a, \dots$$
 (8)

will be the critical external resistance of the machine at the prescribed speed. If any greater resistance than  $x_1$  be intercalated in the circuit the machine will refuse to excite itself, even though there is a small initial magnetization present. So far as there is a weak magnetization present, the machine will act as a feeble magneto-electric machine.

Suppose, now, that x is so far decreased that the total electric resistance is reduced to half its limiting value, that is to say, let  $x' = \frac{1}{2}x_1 - \frac{1}{2}a$ : then the current and the magnetization will both run up until the magnetic resistance is equal to double its initial value, and  $\xi$  will have the value  $\xi' = \alpha$ . The permeability of the magnetic circuit, taken as a whole (iron, copper, and air), will have been halved. This state of things corresponds to the "diacritical point" in the excitation first investigated by the author in 1884; and, if the Lamont-Frölich formula were true, this point would correspond to the state of semi-saturation of the magnetization.

Again, suppose the variable part of the electric resistance to be reduced to zero; in other words, let the machine be short-circuited. Then  $\xi$  will run up to the maximum value it can have at that speed. Calling this value  $\xi_2$ , we have

$$\xi_2 = \frac{4\pi n \text{CS}}{a} - \alpha. \qquad (9)$$

It is further clear that if a fixed value be given to the

external electric resistance x, there will be a limit in speed below which the machine will refuse to excite itself, the leastspeed of self-excitation (called by some authorities the "dead turns," by others the "critical velocity") being given by the equation

 $n_1 = \frac{\alpha(a+x)}{4\pi CS}. \qquad (10).$ 

This throws some light on the observed fact that very small machines are not self-exciting except at very high speeds. The fixed part  $\alpha$  of the magnetic resistance varies in similar machines of different size, inversely as the linear dimensions; also the fixed part a of the electric resistance varies inversely as the linear dimensions of the machine. Hence the least-speed of self-excitation in similar machines (on short-circuit) varies inversely as the square of the linear dimensions. In practice it is possible, in larger sizes of machine, to reduce both  $\alpha$  and a to amounts relatively smaller; for the actual air-space left for clearance may be relatively smaller in large machines, and a relatively greater thickness of copper on the armature-periphery is admissible. When the machine is on short-circuit, x=0, and the last equation then becomes

$$n_1 = \frac{\alpha a}{4\pi \text{CS}} \cdot \cdot \cdot \cdot \cdot \cdot (11)$$

This, too, is important as showing that the least-speed of self-excitation of a machine while short-circuited is a measure of the goodness of the magnetic circuit.

For a shunt-wound dynamo the fundamental equation

becomes

$$(\alpha + \xi) \left( a + s + \frac{as}{x} \right) = 4\pi n \text{CZ}; \quad . \quad . \quad (12)$$

where a is, as before, the resistance of the armature-circuit within the machine, s the resistance of the exciting shunt-circuit, and Z the number of convolutions of the shunt-coil. Excitation does not take place at a given speed n unless x has as its minimum value

$$x = \frac{\alpha as}{4\pi n \text{CZ} - \alpha(a+s)}. \qquad (13)$$

On open circuit, when  $x = \infty$ , the least-speed of self-excitation is

$$n_1 = \frac{\alpha(a+s)}{4\pi CZ}, \qquad (14)$$

the machine then exciting itself through its own circuit as a

series-machine. If short-circuited it will require an infinite

speed to become self-exciting.

There is a still more general way of establishing the rela-Every dynamo may be regarded as an arrangement of two circuits, a primary (or field-magnet) circuit and a secondary (or induced or armature) circuit, between which there is a coefficient of mutual induction M, which is caused to vary by mechanically altering the configuration of the system. If the currents in the two circuits be called respectively  $i_1$  and  $i_2$ , then the work done in starting or stopping either current in the presence of the other is equal to  $Mi_1i_2$ . Now in each revolution of the armature of an ordinary dynamo the current in each of the sections of the armature-coil is twice started and twice stopped. Hence in each semirevolution the work to be mechanically performed in driving is equal to  $Mi_1i_2$ ; or if, as in the series-dynamo, the current in the two circuits is the same, the work to be done is  $Mi^2$ . Now, on the assumption that there is no magnetic leakage, the value of M is equal to  $4\pi S_1 S_2 \div \Sigma \rho$ ; where  $S_1$  and  $S_2$  are the respective numbers of convolutions of the primary and secondary coils which surround the tubes of magnetic force in the magnetic circuit. For our purpose, S2, in ordinary armatures, with symmetrically-wound coils united in a selfclosed circuit, tapped at two opposite points by the two contact-brushes, and with commutation occurring at points where each commuted convolution encloses a maximum magnetic flux, is equal to  $\frac{1}{2}$ C. But the work done by the machine in the electric circuit during a semi-revolution is equal to  $i^2\Sigma R \div 2n$ . Equating this to the work done on the machine gives, as before,

 $\Sigma \rho \cdot \Sigma R = 4\pi n CS$ .

City and Guilds Technical College, Finsbury, June 1888.

LV. Remarks on the Weathering of Rocks, and certain Electrical Phenomena, suggested by some Statements in a popular Novel. By Charles Tomlinson, F.R.S. &c.\*

THE demand for works of fiction has been increasing of late years at so considerable a rate that the chief business of a large circulating library consists in dealing out novels to its subscribers. A cursory examination of the contents of a railway bookstall shows by the gaudy covers of its books that cheap reprints of popular novels form the staple commodity.

<sup>\*</sup> Communicated by the Author.

The monthly magazines, and many of the weekly papers also, deal largely in fiction, the former having two and even three long stories going on in fragments from month to month.

This rage for fiction is such that when young people have finished what is called their education, and can select their own reading, they too often limit their mental efforts to the

perusal of the popular novel;

The effect of this general craving for excitement is as injurious to the mind of the individual as it is to the intellectual progress of the age. If the reading were limited to the works of the great masters of fiction, and the reader strove to study them with a certain critical sense of their value, the result might be wholesome; but a morbid appetite for the sensational literature of the day can only be mischievous.

Some modern writers of fiction, in endeavouring to be realistic, introduce scientific details into their work. If these details were accurate there would be some compensation for the injury inflicted in another direction; but they are in general calculated to give as false views of science, as the other details are often calculated to spoil the appetite for

more wholesome literature.

A writer whose works are just now exceedingly popular has the following astonishing statement, expressed in very ques-

tionable grammar:-

"We perceived a mass of stone was slowly rising from the floor, and vanishing into the rock above, where doubtless there was a cavity prepared to receive it." This stone, weighing thirty tons, is supposed to have been lifted by means of "some very simple lever, which was moved ever so little by pressure on a secret spot."

In another story by the same author, four persons in a canoe in the bowels of the earth receive their supplies of air from that which a river had previously absorbed and then

liberated.

But it may be said that the stories in which these events are recorded are of the Baron Munchausen species, and are so far in keeping with its method. But the same treatment is observed in a quasi-historical novel by the same author, which deals with our contest with the Boers, and the cession to them of the Transvaal. The writer is said to have visited the country which he professes to describe, and yet we have minute details of "mighty columns or fingers of rock, not solid columns, but columns formed by huge boulders piled mason-fashion one upon another."\* One of these is described

<sup>\* &#</sup>x27;Jess,' by H. Rider Haggard, 2nd edit., 1887, p. 43.

as being "some ninety or more feet in height, formed of seven huge boulders, the largest, that at the bottom, about the size of a moderate cottage, and the smallest, that at the top, some eight or ten feet in diameter. These boulders were rounded like a cricket-ball—evidently through the action of water, and yet the hand of Nature had contrived to balance them, each one smaller than that beneath, the one upon the other, and to keep them so. But this was not always the case. For instance, a very similar mass that had risen on the near side of the perfect pillar had fallen, all except the two bottom stones, and the boulders that went to form it lay scattered about like monstrous petrified cannon-balls." (Pages 43 & 44.)

It is amazing to find that a writer who is dealing with real historical events in a land so well known and so often described as the Transvaal, should not have consulted some of the numerous authorities on the subject before he ventured on such a description as the above; but what follows is still more amazing. He is describing an African thunderstorm, pretty much in the style of Burchell, Livingstone, and other authors

of repute, but the following is the writer's own:-

"Suddenly one of the piled-up columns swayed to and fro like a poplar in a breeze, and fell headlong with a crash that almost mastered the awful crackling [?] of the thunder overhead..... Down it came, beneath the strokes of the fiery sword, the brave old pillar that had lasted out so many centuries, sending clouds of dust and fragments high up into the

blinding rain."

Now it is perfectly true that South Africa is in many respects a land of boulders, and is almost a counterpart of Labrador. But there is no known natural process capable of piling up these columns as described above; nor are these boulders waterworn, as the writer supposes. Geologists formerly regarded all boulders as being ice-borne, seeing that they present many of the phenomena of the ice-borne boulders of the Glacial period; but those of the Transvaal differ in being generally rounded, and of local origin, the apparent sources of some of them being from a few to about fifty miles They rest on striated rocks, the crumbling surface of which is moulded into round-backed hillocks. Mr. A. Ramsay accounts for the presence and appearance of these boulders by means of rock slides, and the action of sand driven over them by wind and pressure. But the greater number of the boulders in the Transvaal consist of fragments broken off from the nearly horizontal strata. In many places the valleys are floored with them, the blocks resting on each other in a con-

fused way; and the slopes of many of the hills are strewn with them, while the summits are formed of lavers broken up into separate blocks by weathering. Some of these weathered blocks resemble ruined masonry. Mr. Stow says that in the Kolberg "these shales have been denuded into a remarkably shaped shoulder, jutting out, like the front of a portico. from the mountain-side. They appear to have been left perfectly undisturbed upon the more ancient rocks forming the principal part of the mountain. These latter rocks rise on each side into kopies sixty feet high. Signs of stratification may be seen very distinctly in the hill to the left. Here two of the layers have weathered until their surfaces have assumed a rude columnar appearance. The parts above these, and also those which cap the other kopjes, are composed of rather more coarsely crystalline rocks. They also show lines of stratification; but, instead of the columnar appearance just mentioned, they cleave into immense blocks, piled one on the other, and looking in many places like Cyclopean walls flanking the tops of the hills."\*

It appears from the above details that Mr. Haggard, seeing the weathered mason-like blocks of the hills, supposed them to be built up from the rounded boulders of the older boulder-The old boulder-clay is 1200 feet thick; the boulders are smooth, but are not rounded "like cricket-balls;" and in weathering or falling-out into the valleys they are often piled one on the other to no great height, and they are kept in place by mutual lateral support. The largest are rarely more than six feet across; in short, there is nothing that can give any sanction to the statement that in the Transvaal there are columns formed of ball-shaped boulders which have been rounded by the action of water, and which have subsequently been balanced one on the other. The statement is altogether misleading, and therefore mischievous, and yet this writer persists in it to the end; for at page 330 we read:—"The moon's first rays lit upon one of the extraordinary pillars of

balanced boulders."

In connexion with our present subject may be mentioned a remarkable example of science correcting the views of the antiquaries of the last century, who expended much labour in endeavouring to prove that the rocking stones of Cornwall are Druidical monuments, whereas they are simple cases of weathering. Dr. Paris† many years ago, in describing the Logan or Logging-stone near the Land's End, states that the

<sup>\* &</sup>quot;Notes upon Griqua Land West," Quart. Journ. Geol. Soc. xxx. p. 588 (1874).
† Philosophy in Sport, &c.

granite block, weighing above sixty tons, is so nicely balanced that the strength of one man is sufficient to make it oscillate. He explains how granite disintegrates by weathering into rhomboidal and tabular masses, which by the further operation of air and moisture gradually lose their solid angles and approach the spheroidal form. The upper part of the cliff being more exposed to atmospheric influences than the parts beneath, it happens that these rounded masses frequently rest on tabular blocks; and as the lesser axes of these rude spheroids are perpendicular to the horizon, it is conceivable that some of them may be made to rock on their point of

support.

This subject was further investigated by Mr. Justice Grove, F.R.S., in a paper which I heard him read in Section C of the British Association at its meeting at Norwich in 1868. The following is a very short abstract of his paper. If we suppose a slab of stone lying on another, both having flat surfaces, the attrition and disintegration produced by changes of weather, of temperature, &c., would act to the greatest extent at the corners, and next to them at the edges, because these parts expose respectively the greater surfaces compared with the bulk of the stone. This would tend to round off all the angles and gradually change the rhomb more or less towards an oblate spheroid. If we assume the wearing away between the stones to reach a point which is not in the line of centres of gravity, the upper stone would fall on one side, leaving the unworn point most exposed to be acted on by the water lying in the angle of the crevice, evaporation being less rapid there than at other parts. This point would then be worn away, and the stone would fall back a little, then fresh action upon new surfaces, another oscillation, and so on. Thus, by insensible progression, it becomes not improbable that the last point or line worn away would be the point or line on which, from its being on the line of centres of gravity, the upper stone would rock.

In support of this view the following experiment was tried:—Two parallelopipeds of iron were placed one on the other in dilute acid, which acted on them for three or four days, when the upper one was found to be a perfect analogue of a rocking stone so delicately balanced on two points that it could be made to rock by blowing on it with the mouth. It was observed that the iron rocked only in one direction. Such is the case with the great Logan Stone, and, probably, with most other rocking stones, since it is more likely that a stable equilibrium should be attained on two points than on one. If the surfaces of the stones be in such close contact

that there is no room for the circulation of water, &c., a formation like those near the Cheese Wring will be effected; or if a number of slabs be superposed and the lower ones be more exposed to the weather, so as to catch the dripping and drifting water from the upper, we get a formation like the Cheese Wring, each slab being worn away at the edges, and the lower ones much more than the upper, so that if it does not topple over it may in time end in a Rocking Stone\*.

Another of Mr. Haggard's statements, given as if from actual observation, seems to be nearly as erroneous as in the former cases. He describes a bare strip of *veldt* as being "a very dangerous spot in a thunderstorm, but a great safeguard to the house and trees around it; for the iron-stone cropped up here, and from the house one might generally see flash after flash striking down on to it and even running and zigzagging about its surface." (Page 104.)

In connexion with this statement two questions arise. First, is it really iron-stone, or an ore of iron that crops up at the surface, and if so, secondly, would the line of least resistance be from the cloud to this particular spot, so that the lightning might generally be seen zigzagging over its

surface?

As to the first question, Mr. Penning, in describing the high-level coalfields which cover the eastern portion of the Transvaal, says†:—"The shales and the trap-rocks of course weather very differently, the shales with a flat curve and rounded outline, the igneous rocks, when imbedded, forming steep krantzes, or precipices; when occurring as dykes, with a rough stony outcrop, resembling long lines of waterworn boulders. The rounded form of the loose stones is due to concentric decomposition and weathering; this feature and their brown, frequently glazed, coating, have together given rise to two wide-spread errors—that they are iron-stones, and that they are waterworn."

In the second place, let us consider for a moment the conditions under which a disruptive discharge takes place during

<sup>\*</sup> British Association Report, Norwich, 1868. Trs. of Sections, p. 65. Camphor is sometimes sold in neatly cut parallelopipeds. One of these exposed to the air of my room during several months, first lost its solid angles, then its edges by evaporation, and so passed into a well-shaped oblate spheroid. Two or more of these parallelopipeds piled on each other and exposed to the air, indoors and out, and also to various temperatures and to solvents, gave some interesting results illustrative of weathering; but the details are too lengthy for a note in this place.

† Quart. Journ, Geol. Soc. xl. p. 662 (1884).

The electrified cloud overhead throws a a thunderstorm. corresponding, or even a larger surface of the earth beneath into an opposite electrical state by its inductive action on the intervening dielectric air; and as the tension of the particles of the latter increases by the continued induction of the cloud, the highly charged system at length breaks down, the polarized particles discharge into each other, and there is a flash of lightning, which may strike the earth or a building in one or more places. But before the main discharge takes place, minor discharges, which act as feelers, determine the line of least resistance along which the main discharge travels with a velocity all but infinite; so that it forms to the eye a rippled band of brilliant light, and on reaching the earth disperses so instantaneously that the eye cannot follow it. That the lightning should "generally" strike upon one selected spot "visible from the house," and then be "seen zigzagging over its surface," are statements that must be placed to the credit of the

inventive genius of the novelist.

It has lately been remarked as an extraordinary circumstance that the same church should have been struck three times during thirty or forty years. In all the authentic cases of lightning striking the earth that have come under my notice, I know of no case where the lightning of different storms has struck the same spot; but the lightning of the same storm may strike the earth at or about the same spot many times, as in the following case, namely that of H.M. Ship 'Fisgard' (furnished with Harris's conductors), while at anchor in the Nisqually river in the Oregon territory, in September 1846. From several intelligent reports made by the officers on board, it appears that the ship was struck by a bifurcated discharge of lightning, falling simultaneously on the mainmast and on one of the lower masts with a very loud explosion, but so efficient were the conductors that no injury was done. The report was as if a broadside had been fired from each side of the ship. It was remarked that several of the pine-trees on the neighbouring land were struck and set on fire, and the lightning repeatedly struck the ground in all directions. Some of the men on shore stated that the ship appeared to be coated with fire, and the whole atmosphere to be in a general blaze, with terrific bursts of thunder.

Authentic descriptions of African thunderstorms are somewhat similar in character. For example, that interesting traveller, Burchell, gives several descriptions, of which the following is one:—"The lightning began to flash, and the most tremendous peals of thunder burst over our heads. In an instant, without perhaps more than one minute's notice, a

our confusion." †

black cloud which had formed suddenly emptied its contents upon us, pouring down like a torrent, and drenching everything with water. The parched earth became in the short time of five minutes covered with ponds. The rain ceased as suddenly as it came on, leaving me both startled and surprised at this specimen of an African thunder shower. We passed all at once from the deluged to the arid and dusty ground, the distance of thirty or forty yards being all that intervened between these extremes. Mention had often been made to me, while in Cape Town, of the heavy thunder showers of the interior; but their sudden violence much

exceeded all that I had imagined."\* Livingstone also describes a storm which overtook his party while travelling by night from Linyanti to Seshéke. He says:—"About ten o'clock it became so pitchy dark that both horses and men were completely blinded. The lightning spread over the sky, forming eight or ten branches at a time. in shape exactly like those of a tree. This, with great volumes of sheet-lightning, enabled us at times to see the whole country. The intervals between the flashes were so decidedly dark as to convey the idea of stone blindness. The horses trembled, cried out, and turned round, as if searching for each other, and every new flash revealed the men taking different directions, laughing, and stumbling against each other. The thunder was of that tremendously loud kind only to be heard in tropical countries, and which my friends from India have assured me is louder in Africa than any they have heard elsewhere. Then came a pelting rain, which completed

This excellent observer also describes some remarkable effects of atmospheric electricity on the borders of the Kalahari desert. During the dry seasons which succeed the winter and precede the rains, a hot wind occasionally blows over the desert from north to south. It seldom blows for more than three days at a time, and it has somewhat the feeling of coming from an oven. "This wind is in such an electric state that a bunch of ostrich feathers held a few seconds against it becomes as strongly charged as if attached to a powerful electrical machine, and clasps the advancing hand with a sharp crackling sound. When this hot wind is blowing, and even at other times, the peculiarly strong electrical state of the air causes the movement of a native in his kaross to produce therein a stream of small sparks. The

<sup>\* &#</sup>x27;Travels in the Interior of Southern Africa,' by W. J. Burchell. 2 vols. 4to. (1822-24.)
† Missionary Travels and Researches in South Africa; 8vo, 1857.

first time I noticed this appearance was when a chief was travelling with me in my wagon. Seeing part of the fur of his mantle which was exposed to slight friction by the movement of the wagon assume quite a luminous appearance, I rubbed it smartly with the hand, and found it readily give out bright sparks, accompanied with distinct cracks. 'Don't you see this?' said I. 'The white man did not show us this,' he replied; 'we had it long before white men came into the country, we and our forefathers of old.'"

But it is more to our present purpose to deal with electrical phenomena at or near the earth's surface. Hence I propose to describe some remarkable cases of brush and glow discharge, both of which, according to Faraday, consist of a charging of air, "the only difference being that the glow has a continuous appearance from the constant renewal of the same action in the same place, whereas the ramification is due to a momentary independant and intermitting action of the same kind."\* In other words, a continuous discharge to the air gives the glow, an interrupted one produces the brush,

and in a more exalted condition the spark.

The Geneva correspondent of the Times, in a letter to that journal dated June 20th, 1880, and which appeared on the 24th, speaks of a remarkable electrical phenomenon which appeared at Clarens on the afternoon of the previous Thursday. Heavy masses of rain-cloud hid the mountains which separate Friburg from Montreux, but their summits were lit up from time to time by vivid flashes of lightning. A heavy thunderstorm seemed to be raging in the valleys of the Avants and the Alliaz. No rain was falling near the Lake of Geneva, and the storm still appeared to be distant, when a tremendous peal of thunder shook the houses of Clarens and Tavel. At the same instant a cherry-tree near the cemetery, measuring a metre in circumference, was struck by lightning and shivered into matches. Some people who were working in a vineyard hard by saw the electricity play about a little girl who was gathering cherries, and was already thirty paces from the tree. She is described as literally wrapped in a sheet of fire. The vine-dressers fled in terror from the spot. In the cemetery six persons, separated into three groups, none of them within 250 paces of the cherrytree, were enveloped in a luminous cloud. They said they felt as if they were being struck in the face with hail-stones or fine gravel, and when they touched each other sparks passed from their fingers' ends. At the same time a lumi-

<sup>\*</sup> Experimental Researches in Electricity (1543).

nous column was seen to descend in the direction of Chatelard, and it is stated that the electricity could be distinctly heard as it ran from point to point of an iron railing in the cemetery. None of the persons referred to were hurt, they only complained of an unpleasant sensation in the joints as if they had been violently twisted, a sensation which lasted for a few hours.

A highly electrified condition of the atmosphere may thus produce either the glow- or the brush-discharge. Professor James Forbes, while engaged in his remarkable study of the glaciers of Switzerland, relates that on one occasion near Mont Cervin, the atmosphere being very turbid and the ground covered with half-melted snow, while about 1500 feet below the Col and about 9000 feet above the sea, he noticed a curious sound which seemed to proceed from the alpenstock with which he was walking. He says:—"I asked the guide next me whether he heard it, and what he thought it was. The members of that fraternity are very hard pushed indeed when they have not an answer for any emergency. He therefore replied, with great coolness, that the rustling of the stick no doubt proceeded from a worm eating the wood in the interior! This answer did not appear to me satisfactory, and I therefore reversed the stick so that the point was now uppermost; the worm was already at the other end! I next held my hand above my head, and my fingers yielded a fizzing There could be but one explanation—we were so near a thunder-cloud as to be highly electrified by induction. I soon perceived that all the angular stones were hissing round us like points near a powerful electrical machine. told my companions of our situation, and begged the guide to lower his umbrella, which he had now resumed and hoisted against the hail-shower, and whose gay brass point was likely to become the paratonnerre of the party. The words were scarcely out of my mouth when a clap of thunder, unaccompanied by lightning, justified my precaution."\*

In a paper by H. de Saussure† it is remarked that the lighting up of the rocks at night is analogous to the curious fact of electricity moving over the prairies, as observed by M. Quiquerex near Constamon. It may be compared to a kind of lightning-discharge in miniature, resulting from the electrified cloud brushing over the earth and discharging itself by a thousand sparks coursing over the meadows. Saussure then gives an account of his own observations during

<sup>\* &#</sup>x27;Travels through the Alps of Savoy,' &c. 8vo., Edinb. 1843.
† Phil. Mag. 4th series, xxxv. p. 128 (1868).

thunderstorms on the Nevada de Toluca, in Mexico, and on the Piz Surley, in Switzerland. In the former locality he alludes to the loud rattling or crepitation of the stones, due to electrical discharges. On the summit of Piz Surley he notices certain pricking and burning sensations, and sounds like that of simmering water emitted from sticks laid against the rocks, and the vibrations of the alpenstocks. This humming of the mountains is by no means rare. It seems to indicate a flow

of electricity from the ground into the air.

In a former paper I noticed \* that M. Arago was sceptical as to the existence of ball-lightning. Faraday was equally so. He says:—"That the phenomena of balls of fire may appear in the atmosphere I do not mean to deny; but that they have anything to do with the discharge of ordinary electricity, or are at all related to lightning or atmospheric electricity, is much more than doubtful." † The cases given in my former paper seem to resolve ball-lightning into an exalted case of brush-discharge. Thus, Mr. G. Ambrose Pogson, British Vice-Consul at Hamburg, states in a letter to the 'Times' of June 16th, 1880, that a series of thunder-storms had passed over Hamburg, and that during the 11th inst. the air was densely charged with electricity. "The storm broke about 10.15 p.m., lasting until 11 p.m., during which time at very short intervals from my station, about 1200 yards distance from the copper-roofed tower of the church known as S. Jacobi, about 300 feet high, I saw this phenomenon [which he had previously named St. Elmo's fire apparently resting about thirty feet from the summit of the steeple. The colour was a reddish purple and reminded one somewhat of burning potassium. From repeated comparisons with other objects during the lightning-flashes, I judged these fire-balls (two were several times visible) to be from 4 feet to 6 feet in diameter. The longest duration that I timed was 42 seconds." The appearance and disappearance of these globes of electricity were counted some twenty times: the colour was referred to the glare of the copper roof.

The following also seems to be a case of glow-discharge, described by Mr. Jabez Brown in a letter to the 'Times,' dated Boscastle, December 1st, 1858. He says:—"Last night, at fifteen minutes to nine, ascending one of the sharp hills of this neighbourhood, I was suddenly surrounded by a bright and powerful light, which passed me a little quicker than the ordinary pace of a man's walking, leaving it dark as before.

<sup>\*</sup> See p. 120 of this volume. † 'Experimental Researches' (1641). Phil. Mag. S. 5. Vol. 26. No. 163. Dec. 1888. 2 L

The light was seen by the sailors in the harbour coming in from the sea and passing up the valley like a low cloud."

A very good observer, M. Trécul, relates the following cases \*. During a storm, on the 19th of August, 1880, sparks appeared to proceed from some lightning-conductors, some rising singly and disappearing at a small height, expanding into a circular flash, the light of which diminished from the centre to the In one case two luminous columns rose circumference. simultaneously and parallel, and at a certain height coalesced at right angles. On August 25th, in the same year, during a thunder-storm and in full daylight, he saw a very brilliant body, slightly elongated (say from 30 to 40 centimetres long by 25 cm. broad) and with conical ends, pass from one part of a dense cloud to another. He states that he has often noticed during thunderstorms a band of feeble light momentarily illuminating a street, and reaching right across or only part of the width.

M. Trécul also relates the following curious case:—On the 18th of August, 1876, while writing at an open window, between 7 and 8 a.m., he observed, simultaneously with some loud thunder, small luminous columns descend obliquely on his paper, about two metres long and half a decimetre broad at the widest part; obtuse at the farther end, but gradually thinning towards the table. They had mostly a reddish-yellow tint: near the paper the tints were more intense and varied. In disappearing they left the paper with a slight noise like that produced by pouring a little water on a hot

plate.

Cases of this sort might be greatly multiplied, as also of lightning quitting the conductor. The earliest case of this kind occurs in Franklin's works (vol. i. p. 340), in which an eye-witness relates that "he saw the lightning diffused over the pavement, which was then very wet with rain, to the distance of two or three yards from the foot of the conductor." Franklin very properly remarks on this statement, that "it seems to indicate that the earth under the pavement was very dry, and that the rod should have been sunk deeper till it came to moister earth, and therefore apter to receive and dissipate the electric fluid" (p. 358). He also gives a curious case in which the lightning left the conductor on the outside of a wall to strike the more capacious barrel of a gun resting against the inside of the wall.

I conclude with a few remarks on African thunderstorms, in addition to what has already been said on that subject.

<sup>\*</sup> Comptes Rendus, 1880-81.

Thunderstorms seem to be much more prevalent along the east of Africa than in other parts, and electrical phenomena are most striking in connexion with winds that have traversed arid sandy regions. This is shown in the Kalahari desert. Mr. Wilson remarks\*:—"Towards Basutoland, from November to April, the N.E. wind blows from the shores of the Mozambique and the delta of the Zambesi immense masses of cloud which sweep heavily over the earth, darkening the sky and preceded in their course by dreadful peals of thunder. In the great Namaqua-land, as well as in the desert, rain falls only from thunder-clouds. These rise from the N.E. There is something terribly sublime in a real Kalahari thunder-storm. There are the usual premonitory appearances. At length a cloud of dust approaches, a storm of wind rushes over the plains, a few large spattering drops are heard, and then, with an almost simultaneous blinding glare of lightning and deafening crash of thunder, torrents of mingled hail and rain descend. In a few minutes the country is flooded. In an hour the storm has passed. Moffat states that in this district the lightning is of three kinds: one passing from cloud to cloud; another, forked, passing through the cloud and striking the earth; the third, and most common, is stream-, or chainlightning. It appears to rise from the earth in figures of various shapes—crooked, zigzag, and oblique †, and sometimes like a waterspout at sea; it continues several seconds, while the observer can distinctly see it dissolve in pieces like a broken chain. The perpetual roar of awful thunder on these occasions may be conceived, since some 20 or more flashes may be counted in a minute. The lightning may also be seen passing upwards through the dense mass of vapour, and branching like the limbs of a naked tree on the blue sky above."

Mann ‡ says of Natal, that the thunderstorms are of great intensity, but of short duration; clouds gather over the hill-tops and then spread rapidly out into the valleys. The storm, for the most part, breaks first in the hills and then moves rapidly off towards the east. The lightning is often extremely beautiful, the path of the discharge not unfrequently being seen upon the background of the clouds as a broad quivering ribbon. Paraboloid and elliptical discharges amidst the clouds, with descending or radiating lines setting off from them, are

<sup>\*</sup> Journal of the Royal Geographical Society, xxxv., 1865.

<sup>†</sup> The form is doubtless dependent on the presence of conducting-particles in the air; but, whatever the form, it can only be momentarily or intermittently visible.

<sup>†</sup> Journ. Roy. Geogr. Soc. xxxvii. pp. 66, 67 (1867).

not unusual. Occasionally very interesting streams of horizontal discharge are seen running through the cloud-caps of the Table Mountains just parallel with and above their flat tops. He then becomes eloquent on the varied colours of the lightning, and proceeds to say that "the end of the vast storm-cloud is brought out in deep relief at each discharge by glows of electric light bursting forth from behind its edge, the foldings and twistings of which are rendered conspicuous by lines and sheets of coloured fire. I have seen displays of this character taking place simultaneously on six different points of the horizon, and continuing for hours at a stretch, and I have counted 56 flashes in a minute." Sometimes a number of cattle huddled together are killed at once. "The popular notion is that the discharge runs through the beasts in succession. My own impression, derived from the appearance of the ground where such accidents have taken place, is that the discharge acts at one blow over the entire area covered by the cattle, and divides itself among them."

Highgate, N.

LVI. On Electromagnetic Waves, especially in relation to the Vorticity of the Impressed Forces; and the Forced Vibrations of Electromagnetic Systems. By OLIVER HEAVISIDE.

## [Concluded from p. 449.]

63. CYLINDRICAL Surface of circular curl e in a Dielectric.—Let the curl of the impressed electric force be wholly situated on the surface of a cylinder of radius a in a nonconducting dielectric. The impressed force e to correspond may then be most conveniently imagined to be either longitudinal, within or without the cylinder, uniformly distributed in either case (though oppositely directed), and the density of curl e will be e; or, the impressed force may be transferred to the surface of the cylinder, by making e radial, but confined to an infinitely thin layer. The measure of the surface-density of curl e will now be

$$f = \frac{de}{dz}$$
, = E<sub>(out)</sub> - E<sub>(in)</sub>, . . . . (356)

where e is the total impressed force (its line-integral through the layer). The second form of this equation shows the effect produced on the electric force  ${\bf E}$  of the flux, outside and inside the surface. This  ${\bf E}$  is, as it happens, also the force of the field; but in the other case, when  ${\bf e}$  is uniformly distributed

within the cylinder, producing f=e, we have the same discontinuity produced by f.

H being circular, we use the operator (313). Applying it

to (356) we obtain

$$f = \frac{s}{cp} \left( \frac{J_{0a}}{J_{1a}} - \frac{J_{0a} - yG_{0a}}{J_{1a} - yG_{1a}} \right) H_a; \quad . \quad (357)$$

from which, by the conjugate property (307), and the operator (313), we derive

$$\mathbf{E}_{\text{(in)}} \text{ or } _{\text{(out)}} = \frac{\pi as}{2y} \left[ \mathbf{J}_{0r} (\mathbf{J}_{1a} - y \mathbf{G}_{1a}) \text{ or } \mathbf{J}_{1a} (\mathbf{J}_{0r} - y \mathbf{G}_{0r}) \right] f, \quad (358)$$

$$H_{\text{(in)}} \text{ or }_{\text{(out)}} = \frac{\pi a c p}{2y} [J_{1r} (J_{1a} - y G_{1a}) \text{ or } J_{1a} (J_{1r} - y G_{1r})] f, \quad (359)$$

in which f is a function of t, and it may be also of z. If so, then we have the radial component F of electric force given by

$$\mathbf{F}_{\text{(in)}} \text{ or }_{\text{(out)}} = -\frac{\pi a}{2y} \left[ \mathbf{J}_{1r} (\mathbf{J}_{1a} - y \mathbf{G}_{1a}) \text{ or } \mathbf{J}_{1a} (\mathbf{J}_{1r} - y \mathbf{G}_{1r}) \right] \frac{df}{dz}.$$
 (360)

From these, by the use of Fourier's theorem, we can build up the complete solutions for any distribution of f with respect to z; for instance, the case of a single circular line of curl e.

64.  $J_{1a}=0$ . Vanishing of external field.—Let f be simply periodic with respect to t and z; then  $J_{1a}=0$ , or

$$J_1\{a\sqrt{n^2/v^2-m^2}\}=0,\dots,$$

produces evanescence of E and H outside the cylinder. The independence of this property of y really requires an unbounded external medium, or else boundary resistance, to let the initial effects escape or be dissipated, because no resistance appears in our equations except in y. The case s=0 or n=mv is to be excepted from (361); it is treated later.

65. y=i. Unbounded medium.—When n/v > m, s is real, and our equations give at once the fully realized solutions in the

case of no boundary, by taking y = i,

$$\begin{array}{l}
\mathbf{H}_{\text{(in)}} \text{ or } _{\text{(out)}} = \frac{1}{2} \pi a c n \left[ \mathbf{J}_{1r} (\mathbf{J}_{1a} - i \mathbf{G}_{1a}) \text{ or } \mathbf{J}_{1a} (\mathbf{J}_{1r} - i \mathbf{G}_{1r}) \right] f, \\
\mathbf{E}_{\text{(in)}} \text{ or } _{\text{(out)}} = -\frac{1}{2} \pi a s \left[ \mathbf{J}_{0r} (\mathbf{G}_{1a} + i \mathbf{J}_{1a}) \text{ or } \mathbf{J}_{1a} (\mathbf{G}_{0r} + i \mathbf{J}_{0r}) \right] f, \\
\mathbf{F}_{\text{(in)}} \text{ or } _{\text{(out)}} = \frac{1}{2} \pi a \left[ \mathbf{J}_{1r} (\mathbf{G}_{1a} + i \mathbf{J}_{1a}) \text{ or } \mathbf{J}_{1a} (\mathbf{G}_{1r} + i \mathbf{J}_{1r}) \right] (df/dz), \\
\mathbf{in } \text{ which } i \text{ means } p/n.
\end{array} \right\} (362)$$

The instantaneous outward transfer of energy per unit

length of cylinder is (by Poynting's formula)

$$-\frac{\mathrm{EH}}{4\pi} \times 2\pi r$$

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$$\frac{cn}{8\pi}(f_0\pi am\cos mz J_{1a})^2, \quad . \quad . \quad . \quad (363)$$

if  $f_0$  is the maximum value of f. This may of course be again averaged to get rid of the cosine.

66. s=0. Vanishing of external E.—When n=mv, we make s=0, and then (362) reduce to the singular solution

$$H_{(in)} = \frac{1}{2} r c p f, H_{(out)} = \frac{1}{2} \frac{a^2}{r} c p f, 
 E_{(in)} = f, E_{(out)} = 0, 
 F_{(in)} = -\frac{1}{2} r \frac{df}{dz}, F_{(out)} = -\frac{1}{2} \frac{a^2}{r} \frac{df}{dz}.$$
(364)

Observe that the internal longitudinal displacement is produced entirely by the impressed force (if it be internal), though there is radial displacement also on account of the divergence of e (if internal). Outside the cylinder the displacement is entirely perpendicular to it.

H and F do not alternate along r. This is also true when  $s^2$  is negative, or n lies between 0 and mv. Then,  $q^2$  being

positive, we have

$$E_{\text{(out)}} = \frac{1}{2} a^2 q^2 \left(\frac{2}{8a} J_{1a}\right) [J_{0r} \log qr + L_{0r}] f,$$
 (365)

as the rational form of the equation of the external E when the frequency is too low to produce fluctuations along r.

The system (364) may be obtained directly from (358) to (360) on the assumption that s/y is zero when s is zero. But (364) appears to require an unbounded medium. Even in the case of the boundary condition E=0 at r=x, which harmonizes with the vanishing of E externally in (364), there will be the undissipated initial effects continuing.

If, on the other hand,  $H_x=0$ , making  $y=J_{0x}/G_{0x}$ , we shall not only have the undissipated initial effects, but a different form of solution for the forced vibrations. Thus, using this expression for y, and also s=0, in (358) to (360), we obtain

$$\begin{split} &\mathbf{H}_{\text{(in)}} = \frac{a}{2} \left( 1 - \frac{a^2}{x^2} \right) \frac{r}{a} \, cpe \; ; \quad \mathbf{H}_{\text{(out)}} = \frac{a}{2} \left( 1 - \frac{r^2}{x^2} \right) \frac{a}{r} \, cpe \; ; \\ &\mathbf{E}_{\text{(in)}} = \left( 1 - \frac{a^2}{x^2} \right) e \; ; \qquad \quad \mathbf{E}_{\text{(out)}} = - \frac{a^2}{x^2} e \; ; \end{split}$$

representing the forced vibrations.

67. Effect of suddenly starting a filament of e.—The vibratory effects due to a vibrating filament we find by taking a

infinitely small in (362), that is  $J_{1a} = \frac{1}{2}sa$ . To find the wave produced by suddenly starting such a filament, transform equations (358), (359) by means of (311). We get

$$\begin{split} \mathbf{E}_{\text{(in)}} &= -\left(\pi/2q\right)^{\frac{1}{2}} a \mathbf{J}_{0r} \mathbf{W}_{a}' e, \\ \mathbf{E}_{\text{(out)}} &= -\frac{1}{2} (\pi/2q^3)^{\frac{1}{2}} a^2 \left(\frac{2}{sa} \mathbf{J}_{1a}\right) \mathbf{W} e, \\ \mathbf{H}_{\text{(in)}} &= -(\pi q/2)^{\frac{1}{2}} \frac{ar}{2\mu v} \left(\frac{2}{sr} \mathbf{J}_{1r}\right) \mathbf{W}_{a}' e, \\ \mathbf{H}_{\text{(out)}} &= -(\pi q/2)^{\frac{1}{2}} \frac{a^2}{2\mu v} \left(\frac{2}{sa} \mathbf{J}_{1a}\right) \mathbf{W}' e; \end{split}$$
 (367)

where W is given by (309); the accent means differentiation to r, and the suffix a means the value at r=a.

In these, let  $e_0 = \pi a^2 e$ , which we may call the strength of the filament, and let a be infinitely small. We then obtain

(out) 
$$\left\{ \begin{array}{l} \mathbf{H} = -(q/2\pi)^{\frac{1}{2}} (2\mu v)^{-1} \mathbf{W}' e_0, \\ \mathbf{E} = \frac{1}{2} (q^3/2\pi)^{\frac{1}{2}} \mathbf{W} e_0. \end{array} \right\} \quad . \quad (368)$$

Now if  $e_0$  is a function of t only, it is clear that there is no scalar electric potential involved. We may therefore advantageously employ (and for a reason to be presently seen) the vector-potential  $\mathbf{A}$ , such that

$$E = -pA$$
, or  $A = -p^{-1}E$ ; and  $\mu H = -\frac{dA}{dr}$ . (369)

The equation of A is obviously, by the first of (369) applied to second of (368),

$$\mathbf{A} = \frac{1}{2} (p/2\pi v^3)^{\frac{1}{2}} \mathbf{W} e_0. \quad . \quad . \quad . \quad . \quad (370)$$

Comparing this equation with that of H in (345) (problem of a filament of curl of e), we see that  $f_0$  there becomes  $e_0$  here, and  $\mu$ H there becomes A here. The solution of (370) may therefore be got at once from the solution of (345), viz. (349). Thus

$$A = \frac{e_0}{2\pi v (v^2 t^2 - r^2)^{\frac{1}{2}}}; \quad . \quad . \quad . \quad . \quad (371)$$

from which, by (369),

$$\mathbf{E} = \frac{e_0 v t}{2\pi (v^2 t^2 - r^2)^{\frac{3}{2}}}, \quad \mathbf{H} = -\frac{e_0 r}{2\pi \mu v (v^2 t^2 - r^2)^{\frac{3}{2}}}, \quad (372)$$

the complete solution. It will be seen that

$$\mathbf{A} = \mathbf{E}t + r\mu\mathbf{H}, \quad . \quad . \quad . \quad . \quad (373)$$

whilst the curious relation (353) in the problem of a filament of curl e is now replaced by

$$A = r\mu Z/t, \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (374)$$

where Z is the time-integral of the magnetic force; so that

H=pZ, and curl Z=cE, . . . (375)

Z being merely the vectorized Z. It is the vector-potential

of the magnetic current.

The following reciprocal relation is easily seen by comparing the differential equations of an infinitely fine filament  $e_0$  and a finite filament. The electric current-density at the axis due to a longitudinal cylinder of e (uniform) of radius a is numerically identical with the total current through the circle of radius a due to the same total impressed force (that is,  $\pi a^2 e$ ) concentrated in a filament at the axis, at corresponding moments.

68. Having got the solutions (372) for a filament  $e_0$ , it might appear that we could employ them to build up the solutions in the case of, for instance, a cylinder of longitudinal impressed force of finite radius a. But, according to (372), E would be positive and H negative everywhere and at every moment, in the case of the cylinder, because the elementary parts are all positive or all negative. This is clearly a wrong result. For it is certain that, at the first moment of starting the longitudinal impressed force of intensity e in the cylinder, E just outside it is negative; thus

$$E = \pm \frac{1}{2}e$$
, in or out, at  $r = a$ ,  $t = 0$ ;

and that H is positive; viz.

$$H = e/2\mu v \text{ at } r = a, t = 0.$$

We know further that, as E starts negatively just outside the cylinder, E will be always negative at the front of the outward wave, and H positive; thus

$$-\mathbf{E} = \mu v \mathbf{H} = \frac{1}{2} e \times (a/r)^{\frac{1}{2}}, \quad . \quad . \quad . \quad (376)$$

the variation in intensity inversely as the square root of the distance from the axis being necessitated in order to keep the energy constant at the wave-front. The same formula with +E instead of -E will express the state at the front of the wave running in to the axis. There is thus a momentary infinity of E at the axis, viz. when t=a/v.

So far we can certainly go. Less securely, we may conclude that during the recoil, E will be settling down to its steady value e within the cylinder, and therefore the force of

the field there will be positive, and, by continuity, also positive outside the cylinder. Similarly, H must be negative at any distance within which E is decreasing. We conclude therefore that the filament solutions (372) only express the settling down to the final state, and are not comprehensive

enough to be employed as fundamental solutions.

69. Sudden starting of e longitudinal in a Cylinder.—In order to fully clear up what is left doubtful in the last paragraph, I have investigated the case of a cylinder of e comprehensively. The following contains the leading points. We have to make four independent investigations: viz. to find (1) the initial inward wave; (2) the initial outward wave; (3) the inside solution after the recoil; (4) the outside solution ditto. We may indeed express the whole by a definite integral, but there does not seem to be much use in doing so, as there will be all the labour of finding out its solutions, and they are what we now obtain from the differential equations.

Let E<sub>1</sub> and E<sub>2</sub> be the E's of the inward and outward waves.

Their equations are

$$E_1 = -(a/2q)W_a'Ue, . . . . . (377)$$

$$E_2 = -(a/2q) W U_a'e;$$
 . . . (378)

where U and W are given by (309), the accent means differentiation to r, and the suffix indicates the value at r=a. To prove these, it is sufficient to observe that U and W involve  $\epsilon^{qr}$  and  $\epsilon^{-qr}$  respectively, so that (377) expresses an inward and (378) an outward wave; and further that, by (310), we have

$$E_1-E_2=e$$
 at  $r=a$ , always; . . . (379)

which is the sole boundary condition at the surface of curl of e. Expanding (377), we get

$$E_{1} = \frac{1}{2} \left( \frac{a}{r} \right)^{\frac{1}{2}} e^{q(r-a)} (R+S) \left[ 1 + \frac{3}{y} - \frac{3 \cdot 5}{|2 y^{2}} + \frac{3^{2} \cdot 5 \cdot 7}{|3 y^{3}} - \frac{3^{2} \cdot 5 \cdot 7 \cdot 9}{4 y^{4}} + \dots \right] e, \quad (380)$$

where R+S is given by (309). Now e being zero before and constant after t=0, effect the integrations indicated by the inverse powers of p, and then turn t to  $t_1$ , where

$$vt_1 = vt + r - a$$
.

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The result is

$$E_{1} = \frac{1}{2} e \left(\frac{a}{r}\right)^{\frac{1}{2}} \left[1 + 3z_{1} - \frac{3 \cdot 5}{2} z_{1}^{2} + \frac{1^{2} \cdot 3^{2} \cdot 5 \cdot 7}{2} z_{1}^{3} + \frac{1^{2} \cdot 3^{2} \cdot 5^{2} \cdot 7 \cdot 9}{2} z_{1}^{4} + \dots \right]$$

$$+ \frac{a}{r} z_{1} \left(1 + \frac{3}{2} z_{1} - \frac{3 \cdot 5}{2} z_{1}^{2} + \frac{1^{2} \cdot 3^{2} \cdot 5 \cdot 7}{2} + \dots \right)$$

$$+ \frac{1^{2} 3^{2}}{2} \frac{a^{2}}{r^{2}} z_{1}^{2} \left(\frac{1}{2} + \frac{3}{3} z_{1} - \frac{3 \cdot 5}{2} z_{1}^{2} + \frac{1^{2} \cdot 3^{2} \cdot 5 \cdot 7}{2} z_{1}^{3} - \dots \right) + \dots \right], (381)$$

the structure of which is sufficiently clear. Here  $z_1 = vt_1/8a$ . This formula, when vt < a, holds between r = a and r = a - vt. But when vt > a though < 2a, it holds between r = a and vt - a. Except within the limits named, it is only a partial solution.

70. As regards  $E_2$ , it may be obtained from (381) by the following changes. Change  $E_1$  to  $-E_2$  on the left, and on the right change  $z_1$  to  $-z_2$ , where

$$z_2 = (vt + a - r)/8a$$
.

It is therefore unnecessary to write out  $E_2$ . This  $E_2$  formula will hold from r=a to r=vt+a, when vt<2a; but after that, when the front of the return wave has passed r=a, it will

only hold between r=vt-a and vt+a.

71. Next to find  $E_3$ , the E in the cylinder when vt>a and the solution is made up of two oppositely going waves, and  $E_4$  the external E after vt=2a, when it is made up of two outward going waves. I have utterly failed to obtain intelligible results by uniting the primary waves with a reflected wave. But there is another method which is easier, and free from the obscurity which attends the simultaneous use of U and W. Thus, the equations of  $E_3$  and  $E_4$  are

$$E_3 = -(\pi/2q)^{\frac{1}{2}} a J_{0r} W_a' e, \quad . \quad . \quad . \quad . \quad (382)$$

$$E_4 = -(\pi q^3/2)^{\frac{1}{2}} \frac{1}{2} a^2 \left(\frac{2}{sa} J_{1a}\right) W.e, \quad . \quad (383)$$

by (367); and a necessity of their validity is the presence of two waves inside the cylinder, because of the use of  $J_0$  and  $J_1$ ; it is quite inadmissible to use  $J_0$  when only one wave is in question, because  $J_{0r}=1$  when r=0, and being a differential operator in rising powers of p, the meaning of (382) is that we find  $E_3$  at r by differentiations from  $E_3$  at r=0; thus (382) only begins to be valid when vt=a.

To integrate (382), (383), it saves a little trouble to calcu-

late the time-integrals of E<sub>3</sub> and E<sub>4</sub>, say

$$A_3 = -p^{-1}E_3$$
,  $A_4 = -p^{-1}E_4$ . . . (384)

The results are

$$\mathbf{A_4} = \left(\frac{2}{sa} \,\mathbf{J}_{1a}\right) \frac{a^2 e}{2 \, v} \, (v^2 t^2 - r^2)^{-\frac{1}{2}} . \quad . \quad . \quad (386)$$

From these derive  $E_3$  and  $E_4$  by time-differentiation, and  $H_3$ ,  $H_4$  by space-differentiation, according to

curl 
$$\mathbf{A} = \mu \mathbf{H}$$
, or  $\mathbf{H} = -\frac{1}{\mu} \frac{d\mathbf{A}}{dr}$ . . . . (387)

We see that the value of  $E_3$  at the axis, say  $E_0$ , is

$$E_0 = evt(v^2t^2 - a^2)^{-\frac{1}{2}}; \dots (388)$$

and by performing the operation  $J_{0r}$  in (385) we produce, if  $u=(v^2t^2-a^2)^{\frac{1}{2}}$ ,

$$-\mathbf{A}_{3} = \frac{e}{v} \left[ u + \frac{r^{2}}{2^{2}} \left( \frac{1}{u} - \frac{v^{2}t^{2}}{u^{3}} \right) + \frac{3r^{4}}{2^{2}4^{2}} \left( -\frac{1}{u^{3}} + \frac{6v^{2}t^{2}}{u^{5}} - \frac{5v^{4}t^{4}}{u^{7}} \right) + \frac{45r^{6}}{2^{2}4^{2}6^{2}} \left( \frac{1}{u^{5}} - \frac{15v^{2}t^{2}}{u^{7}} + \frac{35v^{4}t^{4}}{u^{9}} - \frac{21v^{6}t^{6}}{u^{11}} \right) + \dots \right]; \quad (389)$$

from which we derive

$$\mathbf{E}_{3} = \frac{evt}{u} \left[ 1 + \frac{3a^{2}r^{2}}{4u^{4}} + \frac{15a^{2}r^{4}}{2^{2}4^{2}u^{8}} (3a^{2} + 4v^{2}t^{2}) \right. \\
\left. + \frac{5 \cdot 7 \cdot 9a^{2}r^{6}}{2^{2} \cdot 4^{2} \cdot 6^{2}u^{12}} (5a^{4} + 20v^{2}t^{2}a^{2} + 8v^{4}t^{4}) + \ldots \right], \quad (390)$$

These formulæ commence to operate when vt=a at the axis and when vt=a+r at any point r < a, and continue in operation for ever after.

72. Lastly, perform the operation (2/sa)J<sub>1a</sub> in (386), and

$$\begin{aligned} \mathbf{A}_{4} &= \frac{a^{2}e}{2v} \left[ \frac{1}{u} + \frac{a^{2}}{8} \left( -\frac{1}{u^{3}} + \frac{3v^{2}t^{2}}{u^{5}} \right) + \frac{a^{4}}{64} \left( \frac{3}{u^{5}} - \frac{30v^{2}t^{2}}{u^{7}} + \frac{35v^{4}t^{4}}{u^{9}} \right) \right. \\ &+ \left. \frac{45a^{6}}{4.36.64} \left( -\frac{5}{u^{7}} + \frac{135v^{2}t^{2}}{u^{9}} - \frac{315v^{4}t^{4}}{u^{11}} + \frac{231v^{6}t^{6}}{u^{13}} \right) + \dots \right] (391) \end{aligned}$$

from which we derive

$$\mathbf{E_4} \! = \! \frac{a^2 evt}{2u^3} \! \left[ 1 + \frac{3a^2}{8u^4} (2v^2t^2 + 3r^2) + \frac{5a^4}{64u^8} (8v^4t^4 + 40v^2t^2r^2 + 15r^4) \right.$$

+ 
$$\frac{45a^6}{4.36.64u^{12}}(112v^6t^6+1176v^4t^4r^2+1470v^2t^2r^4+245r^6)+\dots$$
 ](392)

These begin to operate at r=a when vt=2a; and later, the

range is from r=a to r=vt-a.

This completes the mathematical work. As a check upon the accuracy, we may test satisfaction of differential equations, and of the initial condition, and that the four solutions

join together with the proper discontinuities.

73. The following is a general description of the manner of establishing the steady flux. We put on e in the cylinder when t=0. The first effect inside is  $E_1 = \frac{1}{2}e$  at the surface and  $H_1=E_1/\mu v$ . This primary disturbance runs in to the axis at speed v, varying at its front inversely as the square root of the distance from the axis, thus producing a momentary infinity there. At this moment t=a/v,  $E_1$  is also very great near the axis. In the meantime E<sub>1</sub> has been increasing generally all over the cylinder, so that, from being \frac{1}{2}e initially at the boundary, it has risen to '77e, whilst the simultaneous value at  $r = \frac{1}{9}a$  is about 95e.

Now consider E<sub>3</sub> within the cylinder, it being the natural continuation of E<sub>1</sub>. The large values of E<sub>1</sub> near the axis subside with immense rapidity. But near the boundary  $E_1$  still goes on increasing. The result is that when vt=2a, and the front of the return wave reaches the boundary, E<sub>3</sub> has fallen from  $\infty$  to 1.154e at the axis; at  $r = \frac{1}{2}a$  the value is 1.183e; at  $r = \frac{3}{4}a$  it is 1.237e; and at the boundary the value has risen to 1.71e, which is made up thus,  $1.21e + \frac{1}{2}e$ ; the first of these being the value just before the front of the return wave arrives, the second part the sudden increase due to the wave-front. E<sub>3</sub> is now a minimum at the axis and rises towards the wave-front, the greater part of the rise being near the wave-front.

Thirdly, go back to t=0 and consider the outward wave. First,  $E_2 = -\frac{1}{2}e$  at r = a. This runs out at speed v, varying at the front inversely as  $r^{\frac{1}{2}}$ . As it does so, the  $E_2$  that succeeds rises, that is, is less negative. Thus when vt=a, and the front has got to r=2a, the values of  $E_2$  are -232eat r=a and -353e at r=2a. Still later, as this wave forms fully, its hinder part becomes positive. Thus, when fully formed, with front at r=3a, we have  $E_2=-\cdot 288e$  at r=3a; -145e at r=2a; and 21e at r=a. This is at the moment when the return wave reaches the boundary, as already described.

The subsequent history is that the wave E<sub>2</sub> moves out to infinity, being negative at its front and positive at its back, where there is a sudden rise due to the return wave  $E_4$ , behind which there is a rapid fall in E4, not a discontinuity, but the continuation of the before-mentioned rapid fall in E<sub>3</sub> near its front. The subsidence to the steady state in the cylinder and outside is very rapid when the front of  $E_4$  has moved well out. Thus, when vt=5a, we have  $E_3=1\cdot022e$  at r=a, and of course, just outside, we have  $E_4=\cdot022e$ ; and when vt=10a, we have  $E_3=1\cdot005e$ ,  $E_4=\cdot005e$ , at r=a.

As regards H, starting when t=0 with the value  $e/2\mu v$  at r=a only, at the front of the inward or outward wave it is  $E=\pm \mu v H$  as usual. It is positive in the cylinder at first and then changes to negative. Outside, it is first positive for

a short time and then negative for ever after.

- 74. We can now see fully why the solution for a filament eo of e can not be employed to build up more complex solutions in general, whilst that for a filament  $f_0$  of curl e can be so employed. For, in the latter case, the disturbances come, ab initio, from the axis, because the lines of curl e are the sources of disturbance, and they become a single line at the axis. But in the former case it is not the body of the filament, but its surface only, that is the real source, however small the filament may be, producing first E negative (or against e) just outside the filament, and immediately after E positive. Now when the diameter of the filament is indefinitely reduced, we lose sight altogether of the preliminary negative electric and positive magnetic force, because their duration becomes infinitely small, and our solutions (372) show only the subsequent state of positive electric and negative magnetic force during the settling down to the final state, but not its real commencement, viz. at the front of the
- 75. The occurrence of momentary infinite values of **E** or of **H**, in problems concerning spherical and cylindrical electromagnetic waves, is physically suggestive. By means of a proper convergence to a point or an axis, we should be able to disrupt the strongest dielectric, starting with a weak field, and then discharging it. Although it is impossible to realize the particular arrangements of our solutions, yet it might be practicable to obtain similar results in other ways\*.
- \* If we wish the solution for an infinitely long cylinder to be quite unaltered, when of finite length l, let at l = 0 and l = l infinitely conducting barriers be placed. Owing to the displacement terminating upon them perpendicularly, and the magnetic force being tangential, no alteration is required. Then, on taking off the impressed force, we obtain the result of the discharge of a condenser consisting of two parallel plates of no resistance, charged in a certain portion only; or, by integration, charged in any manner.

To abolish the momentary infinity at the axis, in the text, substitute for the surface distribution of curl of **e** a distribution in a thin layer. The infinity will be replaced by a large finite value, without other

It may be remarked that the solution worked out for an infinitely long cylinder of longitudinal  $\mathbf{e}$  is also, to a certain extent, the solution for a cylinder of finite length. If, for instance, the length is 2l, and the radius a, disturbances from the extreme terminal lines of  $\mathbf{f}$  (or curl  $\mathbf{e}$ ) only reach the centre of the axis after the time  $(a^2+l^2)^{\frac{1}{2}}/v$ , which may be only a little less, or very greatly less, according as l/a is small or large. If large, it is clear that the solutions for  $\mathbf{E}$  and  $\mathbf{H}$  in the central parts of the cylinder are not only identical with those for an infinitely long cylinder until disturbances arrive from its ends, but are not much different afterwards.

76. Cylindrical surface of longitudinal  $\mathbf{f}$ , a function of  $\theta$  and t.—When there is no variation with  $\theta$ , the only Bessel functions concerned are  $J_0$  and  $J_1$ . The extension of the vibratory solutions to include variation of the impressed force or its curl as  $\cos \theta$ ,  $\cos 2\theta$ , &c. is so easily made that it would be inexcusable to overlook it. Two leading cases will be very briefly considered. Let the curl of the impressed force be wholly upon the surface of a cylinder of radius a, longitudinally directed, and be a function of t and  $\theta$ , its tensor being f, the measure of the surface-density.  $\mathbf{H}$  is also longitudinal of course, whilst  $\mathbf{E}$  has two components, circular  $\mathbf{E}$  and radial  $\mathbf{F}$ . The connexions are

$$-\frac{d\mathbf{H}}{dr} = cp\mathbf{E}, \quad \frac{1}{r}\frac{d\mathbf{H}}{d\theta} = cp\mathbf{F},$$

$$\frac{1}{r}\frac{d}{dr}r\mathbf{E} - \frac{1}{r}\frac{d\mathbf{F}}{d\theta} = -\mu p\mathbf{H},$$
(393)

from which the characteristic of H is

$$\frac{1}{r}\frac{d}{dr}r\frac{dH}{dr} + \left(s^2 - \frac{m^2}{r^2}\right)H = 0, . . . (394)$$

if  $s^2 = -p^2/v^2$  and  $m^2 = -d^2/d\theta^2$ . Consequently

$$H = (J_{mr} - yG_{mr}) \cos m\theta \times \text{function of } t$$
 . (395)

when  $m^2$  is constant, and the E/H operator is

$$\frac{E}{H} = -\frac{1}{cp} \frac{J'_{mr} - yG'_{mr}}{J_{mr} - yG_{mr}}, \qquad (396)$$

material change. Of course the theory above assumes that the dielectric does not break down. If it does, we change the problem, and have a conducting (or resisting) path, possibly with oscillations of great frequency, if the resistance be not too great, as Prof. Lodge believes to be the case in a lightning discharge.

if  $J_{mr}$  or  $J_m(sr)$  is the *m*th Bessel function, and  $G_{mr}$  its companion, whilst the 'means d/dr.

The boundary condition is

$$E_1 = E_2 - f$$
 at  $r = a$ , . . . (397)

 $E_1$  being the inside,  $E_2$  the outside value of the force of the flux. Therefore, using (396) with y=0 inside, we obtain

$$\mathbf{H}_{a} = \frac{\mathbf{J}_{ma}(\mathbf{J}_{ma} - y \mathbf{G}_{ma})}{y(\mathbf{J}_{ma}\mathbf{G}_{ma}^{T} - \mathbf{J}_{ma}^{T}\mathbf{G}_{ma})} cpf$$

$$= \frac{axcp}{y} \mathbf{J}_{ma}(\mathbf{J}_{ma} - y \mathbf{G}_{ma}) f, \qquad (398)$$

where x is a constant, being  $\pi/2$  when m=0, according to (307), and always  $\pi/2$  if  $G_m$  has the proper numerical factor to fix its size.

We see that when

$$f = f_0 \cos m\theta \cos nt$$

when  $f_0$  is constant, the boundary H, and with it the whole external field, electric and magnetic, vanishes when

$$J_{ma}=0.$$

If m=0, or there is no variation with  $\theta$ , the impressed force may be circular, outside the cylinder, and varying as  $r^{-1}$ .

If m=1, the impressed force may be transverse, within the

cylinder, and of uniform intensity.

This is merely chosen as the easiest extension of  $\theta$  and t.— This is merely chosen as the easiest extension of the last case. In it let there be two cylindrical surfaces of f, infinitely close together. They will cancel one another if equal and opposite, but if we fill up the space between them with a tube of conductance K per unit area, we get the case of e circular in the tube, e varying with  $\theta$  and t, and produce a discontinuity in f (which is still longitudinal, of course). Let f be the common value of f just outside and inside the tube; f is then the force of the flux in the substance of the tube, and

 $H_1 - H_2 = 4\pi K(e + E_a)$  . . . (399)

the discontinuity equation, leads, by the use of (396) and the conjugate property of  $J_m$  and  $G_m$  as standardized in the last paragraph, through

$$\left(\frac{H_{1}}{E_{1}} - \frac{H_{2}}{E_{2}} - 4\pi K\right) E^{a} = 4\pi Ke$$

to the equation of  $E_a$ , viz.

$$E_{a} = \frac{4\pi Ke}{-4\pi K + \frac{2cpy}{\pi a} \left[ J'_{ma} (J'_{ma} - yG'_{ma}) \right]^{-1}}, \quad . \quad . \quad (400)$$

from which we see that it is  $J'_{ma}=0$  that now makes the external field vanish.

78. This concludes my treatment of electromagnetic waves in relation to their sources, so far as a systematic arrangement and uniform method is concerned. Some cases of a more mixed character must be reserved. It is scarcely necessary to remark that all the dielectric solutions may be turned into others, by employing impressed magnetic instead of electric force. The hypothetical magnetic conductor is required to obtain full analogues of problems in which electric conductors occur.

August 10, 1888.

LVII. Note by Sir W. Thomson on his Article on Reflexion and Refraction of Light in the November Number.

YESTERDAY evening, in Cambridge, Mr. Glazebrook pointed out to me that the assumption of equal rigidities (§ 14) adopted for the purpose of obtaining agreement with observation, "or at all events on account of its simplicity," is necessary for stability, on the peculiar assumption of zero velocity for condensational-rarefactional wave which I intro-This, which I had not noticed previously, is most satisfactory. It is satisfactory to find an assumption, which was adopted arbitrarily for the sake of results, thus now demonstrated as an essential of the theory. The proof of instability unless B=B' is obvious if we consider, for example, a globe of elastic solid of quality (A', B') embedded in an infinite solid of quality (A, B). Let the interfacial spherical surface be caused to expand infinitesimally from radius a to radius a(1+e), and be held so by force applied to it, with the matter all in equilibrium outside and inside; while we calculate the force required to hold it so. Taking coordinates from the centre as origin, we have, for the component displacements of the matter within the interface.

$$u = x(1+e), v = y(1+e), w = z(1+e);$$

whence, by (7) of § 9, we find for the force per unit area with

which the matter within pulls the interface,

$$(A' - \frac{4}{3}B') . 3e.$$

And for the component displacements of the matter outside the interface, we have

$$u = e^{\frac{a^3x}{r^3}}, \quad v = e^{\frac{a^3y}{r^3}}, \quad w = e^{\frac{a^3z}{r^3}};$$

whence, by (7) of § 9, we find for the force with which the matter without pushes the interface,

Hence the sum of inward push from without and inward pull from within, on the interface, is

$$3[A' + \frac{4}{3}(B - B')]e$$
.

Hence for stability, or at least lability, it is necessary that  $A' + \frac{4}{3}(B - B')$  be positive, or at least zero. Hence if A' = 0, we must have  $B \ge B'$ . And if A = 0, we find, similarly, by considering a case in which a portion of (A, B) solid is embedded in (A', B') solid, that  $B' \ge B$  is necessary for stability or lability. Hence for stability or lability, if A = 0 and A' = 0, we must have B = B'. The question does this suffice for stability, or at least lability, is not answered by mere consideration of the preceding spherical example: but that it does suffice follows from §§ 4, 5 of the Article.

Mr. Glazebrook also yesterday evening showed me that my hypothesis of zero velocity for condensational-rarefactional wave allows the Stokes-Rankine-Rayleigh hypothesis of aelotropic effective inertia to become valid for the explanation of double refraction with exactly Fresnel's wave-surface, and with velocity of propagation depending properly on the direction of the vibration; but with the direction of vibration perpendicular to the ray-direction: instead of being in the tangent-plane to the wave-surface as in Fresnel's theory, and as it essentially is in any theory which supposes the ether to be an incompressible solid. He promises a paper on this subject for the December Number of the Philosophical Magazine.

W. T.

Train, Cambridge to Glasgow, November 1, 1888. LVIII. On Figures Produced by Electric Action on Photographic Dry Plates. By J. Brown\*.

[Plates VI. & VII.]

WHILE photographing the electric discharge from an induction-coil it occurred to me to try what effect would be produced on the plate by the discharge when taking place

directly on the sensitive film itself.

A rather rapid photographic dry plate was laid film upwards on a piece of sheet metal connected to one terminal of the secondary, whose ordinary discharging points were set about 3 centim. apart to act as a by-pass to the spark and prevent it striking over the edge of the plate. The end of a wire from the other terminal rested on the centre of the film. A single discharge from the coil was caused by moving its mercury-break by hand, and the plate was then placed in the developer.

When the terminal wire at the centre of the plate was negative, and particularly if no discharge passed over the edge of the plate, the result was like that represented at A (Plate VI.), which shows the typical negative form consisting of beautiful sharply defined symmetrical palm-like fronds on irregular stems branching out from the centre where the wire rested, together with a mass of less distinct irregular straggling lines also branching outwards, but not reaching so

far as the fronds.

When the wire terminal was made positive and a discharge caused under otherwise precisely similar conditions, the figure was quite different, as in B, and consisted on the plate of dark irregular branchings sharply defined except near the centre, where apparently the luminosity of the spark has caused a nebulous edge to the branch. These branchings are accompanied by light irregular straggling radiations, similar to those on the negative plate, but having a rather more distinctly centrifugal direction and extending beyond the well-defined branches, from which they seem to be to some extent off-shoots. The experiments were repeated several times and gave similar characteristic results. If, however, the metal sheet were omitted, and wires from both positive and negative terminals brought down on a plate insulated on a paraffin block, neither the palm-fronds on the negative, nor the dark markings on the positive appeared, but only the lighter irregular branchings. and these were in much greater quantity round the positive

<sup>\*</sup> Communicated by the Author.

terminal than at the negative; but with the poles not too far apart they stretched across from one to the other in the form

of confused and irregular lines of flow.

When the plate was laid as before on a metal sheet and wires from both positive and negative terminals brought down on the film, a discharge produced the characteristic figures under their respective wires. These were best defined only when no spark discharge crossed between the wires on the plate; and there was in this case no branching out of the positive and negative markings towards each other, the inductive circuit sensibly completing itself through the metal sheet under the plate.

When the difference of potential was made sufficient to produce spark-discharge between the terminals on the plate, the resulting marking depended in several respects on the

presence or absence of a metal sheet under the plate.

With no metal sheet, and the plate insulated on a block of paraffin, the discharge took a fairly direct course between the terminals C (Plate VII.), with only slight crookedness, but sometimes in a double line. On this plate the characteristic palm-fronds of the negative and dark branchings of the positive pole are wanting, and the lighter tracery forms a rough indication of confused lines of flow between the poles.

With a sheet of foil pasted on the back of the plate (leaving a margin of about 2 centim. round the edge) and spark-discharge between the terminals, there is exceedingly little, if any, distinct tendency of the positive and negative markings towards each other. The track of the main spark is very crooked, meandering over the plate in a quite irregular way, and making sometimes sharp distinct angles in its course. From about half of its length from each end, but principally from the terminals, branch off here and there the characteristic positive or negative markings. D, E, and F (Plate VII.) are examples, the latter being the result of half a dozen sparks passed over a plate in succession from a pair of terminals resting on it.

When a strip only of foil was fixed on the back of the plate so that its length crossed the line joining the poles at an angle of about 45°, as at G (Plate VII.), where the rectangle shows the position of the foil, and about twenty sparks were passed, they all took a similar S-shaped course, having been apparently attracted out of the direct line to follow that of the foil

underneath the glass.

The meandering form and general appearance of these sparks, when acted on inductively by the foil under the plates, remind one very much of certain kinds of lightning-flashes,

and suggest at least a possibility of some similarity in the

causes producing each.

The question now arose as to whether the result was due to a photographic effect of the luminosity of the spark, or to some more direct action of the discharge on the film—to what might be called an "electrographic" action.

As evidence for the latter view came the apparent insufficiency of the light, actually visible when the discharge took place, to produce the effect. The lighter branchings were not to me visible at all in either positive or negative, and only an

indication of the frond formations in the negative.

There are also in the positive plate B (Plate VI.) several intervals as if the spark had not been in immediate contact with the film, but had passed over it, leaving only a foggy mark instead of a sharply defined black line. The break or interval would scarcely have been so marked if the whole effect were photographic only.

However, to further investigate this question the discharge was taken with the two terminals on the back or uncoated side of the plate. The figures which now appeared on the film were quite different from those described above. case there was impressed on the back of the film (next the glass) the cloudy photographic effect of the branching discharge on the back of the plate.

On the front or outer side of the film under the positive terminal the figure reminded one of a photograph of a maidenhair fern out of focus. That under the negative is a collection of peculiar tadpole-like markings, whose general arrangements correspond in size and shape to the fronds formed by the discharge on the back of the plate. These figures would

appear to be due to electricity induced in the film.

To try further the effect of induction on the film, I cut my initials in tin-foil after the manner of a stencil plate, placed the foil on the film, a piece of gutta-percha tissue on the foil, and pressed all together in an ordinary photographic printing frame. A second piece of foil was placed on the back of the plate, leaving a margin all round, and the foils were joined to opposite poles of the coil with its terminals giving a bypass of about 1 centim., so as not to have any spark discharge over the plate. The result with the poles connected in either sense, and the coil working for about a minute was, with the stencil foil either positive or negative, an irregular blackening all round the edge of the foil, including the edges of the cut-out parts as if a discharge had passed out from the edges. In some places the characteristic markings of positive or negative, as the case might be, were visible. There was, however,

a slight visible discharge from the edge of the foil on the back of the plate, and probably therefore the same from that on the film to which the edge-marking may be due. There was also on the plate much blotchy marking, apparently corresponding to the wrinkling of the foil in contact with the film.

With a piece of gutta-percha tissue between the stencilplate foil and the film, the result was similar, only the line round the edges was narrower and the blotching less marked, hence the initials came out more distinctly. When four thicknesses of gutta-percha were interposed, there appeared only

blotchy markings on the part under the foil.

These results would go to show that actual disruptive discharge over or in the film is not needed to produce an effect visible on development, but that the figures are produced partly at least by direct electric action on the sensitive film without the intervention of a visibly luminous action, or what would be usually understood as a purely photo-chemical cause. Possibly further investigation may show that we have here a new kind of experimental evidence on the relation of electricity to light.

I may add that it is necessary, especially in the experiments with the terminals on the back of the plate, to use rather sensitive plates; "60 times" plates do very well, while slow plates give imperfect figures in all cases and show almost

nothing with the terminals on the back.

## LIX. The Invisible Solar and Lunar Spectrum. By S. P. Langley\*.

THE following investigation has been made from studies at the Allegheny Observatory; but it is proper to state that the provision of the very special apparatus used is due to the liberality of a citizen of Pittsburgh, who has desired that his name should not be mentioned.

This paper is an abstract of a forthcoming memoir, which will eventually appear in the fourth volume of the publications of the United States National Academy of Sciences, to which

the reader is referred for fuller details.

\* Communicated by the Author, to whom we are likewise indebted for the clichés.

As the writer has already presented to the National Academy a memoir (read October 17, 1884, Memoirs Nat. Acad. of Sci., vol. iii.) on the heat of the moon, in which he spoke of investigations still in progress on it, it should be said that these are not yet published, and that they are only given here so far as is necessary in explanation of certain anomalies in the infra-red solar-heat spectrum, which forms the principal subject of the present paper.

Ever since the writer first\* investigated the infra-red of the solar spectrum to the extent of about three microns, he has assumed, from all analogy, the probable existence of solar heat of still greater wave-lengths, which, however, he has not till lately been able to experimentally demonstrate; so that there has been a doubt whether such waves were emitted by the sun after absorption by its own atmosphere, or whether they existed previously to absorption by the earth's atmosphere, and, owing to the action of the latter, never reached us. Below the point  $2^{\mu}$ .8, to which the maps published in 1882 and 1883 extended, it was stated, however, at that time that there had apparently been detected feeble, or, more properly speaking, dubious, indications of solar energy. This doubt arose partly from this extreme feebleness here of the heat itself, partly from lack of the usual experimental means, since the glass of our prisms (which, as we had discovered, transmitted the greater part of all the sun's invisible heat then known) absorbed this, while no maker could then supply its place with suitable rock-salt; and, most of all, from a difficulty of a less familiar kind, but which should from its importance be clearly apprehended by the reader. This is, that even if we could recognize that some feeble invisible heat existed, there were then no means of determining that it really belonged to the part of the spectrum where it was found, and was not intruded invisible heat of a more refrangible kind, diffused from its proper place in the upper spectrum by the inevitable action of the spectroscopic apparatus.

In 1884 and 1885, while investigating the invisible spectrum of the sunlit side of the moon, we first found evidence of heat in this region from any extra-terrestrial source—heat whose enormous wave-length was comparable to that chiefly radiated from ice, which was also experimented on. This was so far distinct from the reflected solar heat of greater refrangibility, which occupied its own part of the spectrum, that our experiments indicated that it was chiefly not reflected, but radiated from a surface at a low temperature. But the chief anomaly was that, while we had thus definitely recognized this kind of heat in the extremely feeble heat-spectrum of the moon, we had not yet done so in the far stronger solar one, or, as I observed at the time, that "we here seem to have heat from the moon of lower wave-length than from the sun."

I do not state (it must be observed) that the sun's heat here is less than the moon's, but that what there is is harder to

<sup>\*</sup> Comptes Rendus de l'Institut de France, September 11, 1882. Amer. Journ. of Science, March 1883; Phil. Mag. March 1883.

recognize. It is not easy to give an adequate idea of the difficulties of observation which lead to this apparently paradoxical result, particularly as physicists are so far from having yet investigated this region that even the barriers which have closed it to research are themselves of an unfamiliar kind. I can perhaps best illustrate it by analogy. Every spectroscopist knows how very hard it is to view the lines below A; and that even A itself, though very large, is not an easy object to see without special precautions. This arises not so much from the fact that the very deep red light here, like that of dull glowing iron, feebly affects the eye, but, in a still greater degree, because vellow and orange light exists in relatively enormous quantity in the neighbouring parts of the visible spectrum, and that irregularly diffused and reflected portions of this light reappear where they do not belong and overpower the radiation legitimately there. Still we can put a coloured glass before the slit and cut off the intruding light in a great measure, and we can see the extraneous light which comes in, and allow in some degree for its effects; but here, in the actual case of the unseen heat in the far more remote spectral region we are about to describe, all radiations, both the feeble ones we would study, and the intruders on them which we would avoid, are alike invisible, and we are, of course, unable in any case to use glass, since this is opaque to all the rays now in question. If any one familiar with the visible spectrum will imagine himself as trying to discriminate with his eyes shut between these different components of the apparent radiation just below Fraunhofer's A, and endeavouring while blindfold to say how much of it legitimately belongs there and how much does not, he will have a better conception of the difficulties peculiar to our actual field of research, though still an inadequate one, since the total heat radiation here is at best less than the hundredth part of that in the vicinity of the A line, which we have used in illustration.

For the clearer understanding of this I must, in anticipation of what follows, remark that while in the solar spectrum the maximum heat, as we all know, appears not very far from the red, so that the heat corresponding in a general sense to the short waves is great, and to still longer ones small, in the lunar invisible spectrum the reverse is the case; for here, speaking generally, the solar reflected heat found in the upper part of the lunar spectrum is less than the heat apparently radiated from the moon's own soil, which is of great wavelength, and which we have found in the extreme region of the spectrum we are now studying. In other words, the typical solar-spectrum heat is greatest in the relatively short wave-

lengths; the typical lunar-spectrum heat is greatest in the long wave-lengths. The explanation of the curious fact that this particular quality of heat may be more easily recognized where it exists in a less degree as in the lunar spectrum than where it is found in a relatively great degree as in the solar. will be still clearer if we consent (in continuance of the illustration) to further compare this lunar invisible radiation of great wave-length to the deep-red light from a piece of scarcely luminous hot iron. This peculiarly deep red is seen with little difficulty in the iron in a dark room, but never in daylight; yet it is of a quality which we know from theory must exist in far greater degree in the daylight itself; nor do we, even when we would isolate it in a certain part of the solar spectrum, see it there, because it is now obscured by the inevitable diffusion or reflexion of part of the neighbouring brilliant light which the prism ought to keep wholly away, but (owing to inevitable instrumental defects) does not. dull glowing iron carries no white light along with it, and therefore its feeble peculiarly deep red is easier seen than the far stronger corresponding red in the solar spectrum.

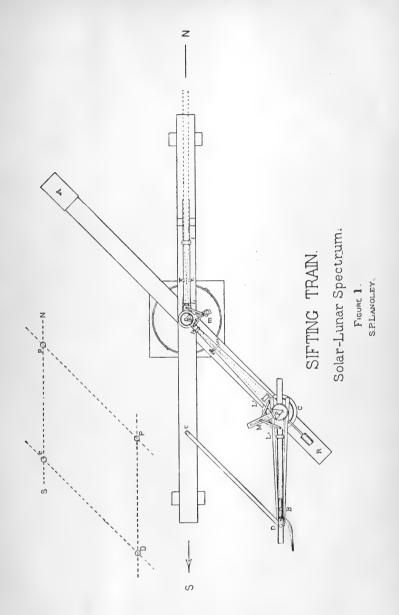
By the aid of this analogy in the case of light, and passing now to the actual case of wholly invisible radiation, I hope it may be clear how the feebler heat in the lunar extreme infrared spectrum was at first recognized more easily than the

stronger corresponding heat in that of the sun.

It may be asked why (if we cannot cut off the diffused heat in the solar infra-red spectrum by the use of an absorbing glass) we cannot put a prism in front of the slit after the plan of Helmholtz. This is practically impossible here (owing to instrumental conditions which we need not now explain), unless we find some way of keeping the axis of the spectrobolometer either motionless or always parallel to itself, in spite of the varying direction of the rays from such a prism, and of automatically limiting the kind of radiation to be observed in any part of the spectrum, to that legitimately The following arrangement was, after belonging there. various trials, adopted with success. Its immediate purpose is to overcome the difficulty which we have just explained at such length—that is, to sift out the extraneous heat which remains after the ordinary action of the prism; but it can of course be used for light also.

## Description of Sifting Train (see fig. 1).

Let NS be a massive beam, resting on two piers, and immovably fixed in the meridian. Let AR be a second beam, movable on a turn-table, placed centrally beneath NS.



Temporarily mounted on A R, and moving about with it, is the large spectro-bolometer described in a previous memoir. The centre of its graduated circle (C) lies under the point P. Its two long arms are not free to move as usual, but are constrained by mechanical attachments (not here shown) to

occupy the positions Pp, PD.

Two large  $60^{\circ}$  prisms of the same material (pure rock-salt from the same mine), their faces worked with the greatest accuracy, are placed with their equal refracting angles in opposite directions, one (P) at the obtuse, the other (p) at the acute angle of the parallelogram (PpDc), the vertices of all whose angles in the mechanical construction are pivoted and connected by inflexible arms, so that (both prisms being kept automatically in minimum deviation by the attachments, Mm) the angle of minimum deviation (cpP) for the first prism is necessarily equal to the angle of minimum deviation (RPD,

or its equal PDc).

Thus, if the pencil of solar lunar heat (reflected from a large siderostat on the north, not shown here) passes from N towards S, on moving the beam AR, pivoted at p (p being the projection in our drawing of a vertical line passing through the centre of the turn-table and the median line of NS and AR) into various positions (NS remaining fixed), the rays, which are refracted by the prism p in the direction p P, will emerge from P in the direction P D and fall upon the bolometer B. A condensing-lens (l) forms the solar image on the slit  $(s_1)$  of the first spectroscope, whose train (consisting of collimator,  $l_1$ , prism, p, and image-forming lens,  $l_2$ ) forms a spectrum on the slit  $(s_2)$  of the second spectroscope. Here a narrow pencil from the first spectrum, comprising only the particular wave-lengths which fall within the width of  $s_2$ , is admitted, and, by the second train  $L_1 P L_2$ , formed into a horizontal spectrum at and on either side of B. When we move AR this spectrum moves in turn past the vertical linear thread of the bolometer B, which lies in the focal plane of this spectrum, and is immersed in its successive absorption-lines as these defile past it. The function of the first spectroscopic train  $(l, l_1, p, l_2)$  is solely to sift out the extraneous radiations, and to present at the second slit  $(s_2)$ only those which legitimately belong to that part of the spectrum we wish to study. These pure rays pass into the second slit and are analysed by the second train in the usual way, by the aid of the linear bolometer at B, and of the circle (C) reading to ten seconds of arc.

The objection to this apparatus is its complexity, which, however, we have been unable to advantageously diminish.

We may, however, satisfy ourselves by visual observation of the Fraunhofer-lines seen through the whole compound system (entirely of salt) both of the optical perfection of the surfaces of our entire double train, and of the accuracy of its purely automatic action.

## Results of Observation.

With this and the apparatus already described in previous memoirs we have searched the extreme infra-red solar spectrum, at first without definite success, later with results which will be better understood by the accompanying drawings. Fig. 2b shows the newly investigated invisible solar-heat spectrum on the normal scale up to an (estimated) wavelength of 18<sup>th</sup>. Fig. 3a is an enlarged view of that portion of it extending to 5<sup>th</sup>, and fig. 3b a photographic interpretation of the last, obtained automatically by a special device; so as to present somewhat the appearance which this heat-region might be expected to show to an eye which could see it.

Inordinately long as our new chart (fig. 2b) may seem, we see that the scale is, nevertheless, contracted to the last degree, so that the entire visible spectrum is compressed into hardly an inch, seen on the left or violet end. Next we have the already described solar infra-red, already shown to exist to  $2^{\mu}$ ·8, and which includes its great absorption-bands  $\Phi$ ,  $\Psi$ ,  $\Omega$ ,

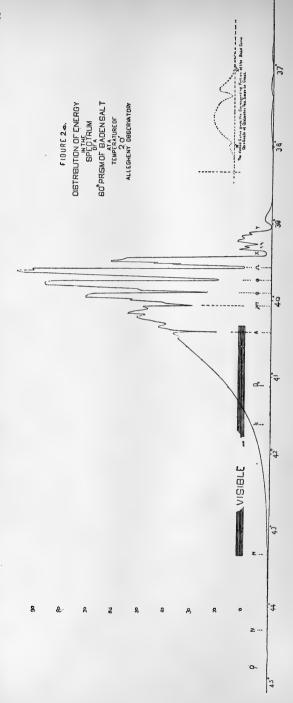
already investigated with glass prisms.

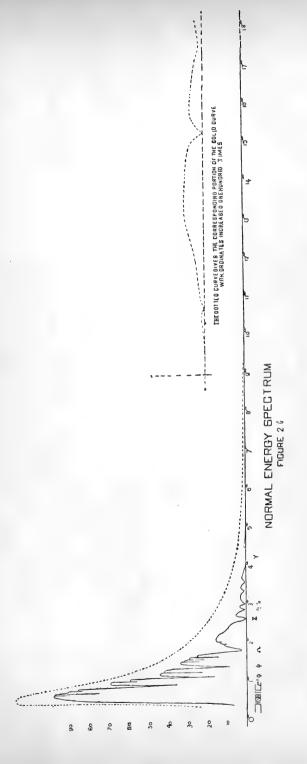
The principal lunar heat lies chiefly beyond the great wavelength of 0.01 millim.  $(10^{\mu})$ , and ere we reach it we pass over a region between  $5^{\mu}$  and  $11^{\mu}$  (many times the length of the entire visible spectrum), where the solar heat seems to have been, to our present means of recognition, entirely absorbed, probably chiefly by our own atmosphere.

It will be convenient, however, after noting the extent of the whole region shown in fig. 2a, to commence our description with the detailed portion shown in figs. 3a and 3b, to which the reader is referred in illustration of what imme-

diately follows.

The lowest bands already described, as seen in the spectrum of a flint-glass prism, are the small ones  $\omega_1$  and  $\omega_2$  near  $2^{\mu}$ . Below this point all is believed to be here given for the first time. The bands in this new region are undoubtedly due chiefly, if not wholly, to telluric absorption; and they are notably variable, depending on the season of the year, and still more on the hour of the day. As the sun sinks, its rays, passing through increasing air-masses, suffer absorptions which singularly change the appearance of the bands, as is shown in figs. 4 and 5, which, however, are drawn upon the





prismatic, not the normal, scale. They are identifiable with

the portion extending from X to Y on the latter.

Observations made during the winter indicate that the band at  $2^{\mu}.64$  (figs. 3 a, 3 b) is, with a high sun, largely filled up, especially on the less refrangible side. At noon a subordinate maximum has been found within the low sun limits of this band at  $2^{\mu}.94$ , and a second one at  $2^{\mu}.80$  frequently accompanies it, producing subordinate minima at  $2^{\mu}.89$  and  $3^{\mu}.02$ .

As the absorption increases, with a sinking sun, these subordinate maxima disappear to a very great extent, that at  $2^{\mu}$ ·80 being the first to vanish as well as the quickest to grow, so that at noon, on a cold day, it not only surpasses the maximum at  $2^{\mu}$ ·94, but even begins to approach that at  $3^{\mu}$ ·20, while, when the sun's altitude is less than  $10^{\circ}$ , the nearly uniform part of the band extends from  $2^{\mu}$ ·45 to  $3^{\mu}$ ·15 without a break. Minor cold bands at  $3^{\mu}$ ·37 and  $3^{\mu}$ ·69 are suspected. The evidence for their existence may be seen by inspecting the high sun and low sun curves given in fig. 4. From  $4^{\mu}$ ·0 to  $4^{\mu}$ ·5 we have another region of almost complete absorption, followed by a maximum at  $4^{\mu}$ ·6, beyond which lies the longest break of all, stretching from  $5^{\mu}$  to  $11^{\mu}$ .

The solar heat throughout the region from 5" to 11" is probably far greater than it here appears, and if the parts struck out by our atmosphere were restored it would probably be found that a not wholly inconsiderable portion of the sun's heat lies in this region; for it must be borne in mind that even the maxima are doubtless in some degree affected by a linear absorption, so that, because a part of the spectrum appears to be almost entirely transmitted, we cannot infer that it necessarily is so, or that it has not, after passing through the upper strata of the air, already parted with a considerable

portion of its energy.

While the position of a line or band caused by light from the centre of the sun is, in the upper spectrum, unchangeable, in this extreme low spectrum (if we could photograph it, like the upper, on cold and on hot days, with high sun and with low) the absorption would be seen to increase not symmetrically with the centre of the band, but more on one side than the other, so as to considerably modify the position of greatest absorption. This seems to be the explanation of a curious fact which could not have been anticipated in advance of observation; that is, that the centres of several of these bands and lines are under some conditions found to be shifted to a recognizable extent, and hence their wave-lengths are, within certain limits, variable.

It seems as though the absorption, which we see exercised

M το 5<sup>μ</sup>.

ETER IN 1886, AT THE

RVATORY.

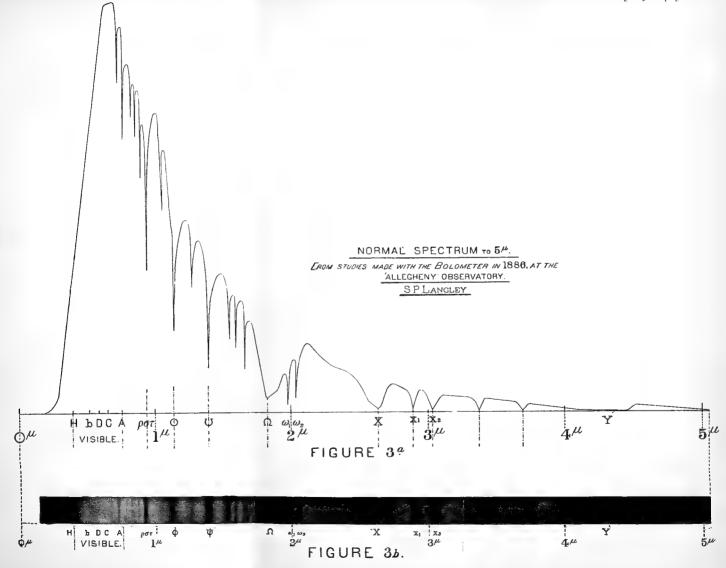
4<sup>μ</sup>

5<sup>μ</sup>

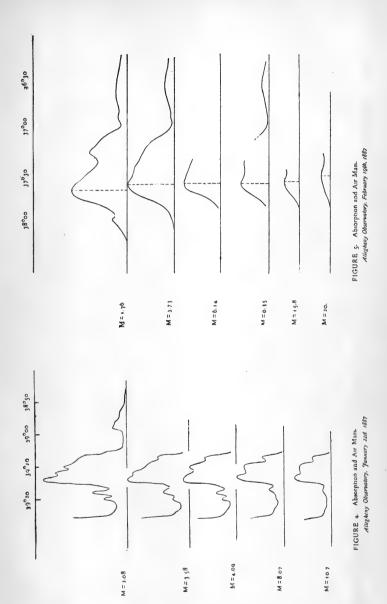
4<sup>μ</sup>

5<sup>μ</sup>









in most of the visible spectrum by fine lines, which begin already to show aggregation into a broader absorption-band on the borders of the infra-red (e.g. the well-known "A" of Fraunhofer), is, as we pass further down into the invisible part, represented by wider and wider bands, like  $\Phi$ ,  $\Psi$ ,  $\Omega$ (composed themselves probably of lines). The heat between these local regions of almost total absorption continues as I have repeatedly before stated, to be (contrary to the old belief) apparently transmitted with even greater facility than that in the visible spectrum. These bands have grown larger and closer and closer together as we have come down from the visible spectrum below the point where the old map ended, and not far below 5" they seem to practically coalesce into one almost unlimited cold band. We do not, let it be observed, assert that the absorption is absolutely total even here, and, in fact, there is always a feeble heat to be observed throughout this extent. This, however, the use of the sifting train shows to be largely, at any rate, factitious, but we admit the possibility that subsequent research may prove that it is not all so.

Let us now recur to fig. 2b, where we shall find below  $10^{\mu}$  the same dependence of the effects upon the season and

the hour, as in the part above  $5^{\mu}$ .

At  $10^{\mu}\cdot 2$  observations made during the autumn showed scarcely the feeblest suspicions of heat, and the same has held good in the very mild weather of the past winter (of 1887); but on a few days, when the temperature had fallen below the freezing-point, a notable maximum was found at this point, followed by a minimum at  $10^{\mu}\cdot 7$ . The height of this maximum relatively to the principal one in this region at about  $13^{\mu}$  appears to be correlated with the composition of the air as affected by the temperature. On the coldest day (temperature at noon  $-6^{\circ}\cdot 7$  C.) the deflection at midday for  $\lambda = 10^{\mu}\cdot 2$  was nearly one-half that at  $13^{\mu}$ ; but on other days, when the temperature was near  $0^{\circ}$  C., the deflection at  $10^{\mu}\cdot 2$  did not exceed one-fourth that at  $13^{\mu}$ , while at temperatures above  $+10^{\circ}$  C. it was not noticeable.

It is in the region near  $13^{\mu}$  to  $14^{\mu}$ , or over twenty times the length of the visible spectrum below it, that we have found the maximum of the lunar heat-spectrum; and it is here that we first obtained indications of solar radiation corresponding in its great wave-length to this special lunar radiation, but of amounts nonestimable by the means till now employed. I have already spoken of its almost unrecognizably small amount, and a perhaps more vivid apprehension of its extreme minuteness will be gained from the statement that on this graphical construction, on the scale of ordinates used in delineating the curve from

0 to  $5^{\mu}$ , no heat appears below  $5^{\mu}$  anywhere, not even at the maximum near 13<sup>\mu</sup> and 14<sup>\mu</sup>; because, though heat exists to the bolometer, the highest ordinate which would represent it on our drawing is not so great as the thickness of the thin black line, which denotes the axis of abscissæ. I have accordingly here been obliged to exhibit it separately by a dotted curve whose ordinates are one hundred times those in the remainder of the spectrum. The points of minima in it are identifiable with absorption-bands, which we have directly observed and which we have independently found to exist in our own atmosphere by studying the radiations from a copper surface, one metre square, at the temperature of boiling water placed in the open air at a distance of one hundred metres from the bolometer. (The description of this will be found in a supplementary research to be given elsewhere.) The principal lunar heat, then, is found here, at a point of the spectrum corresponding to the maximum radiations from melting ice, but its maximum amount is probably less than 1 per cent. of the corresponding solar heat which we have just found to be itself so small. That we can detect the lunar heat at all under these circumstances is due to the fact that we are here able to employ for it very short-focused mirrors and lenses, which condense it into a very short and relatively hot spectrum (there being no fear of their diffusing extraneous heat, since none worth mention exists). In the case of the sun we must employ a wholly different optical train, forming a far longer spectrum. It would be easily understood that these means, which enable us to determine the position of the solar and lunar heat-maxima here, are not favourable to a determination of the relative amounts of heat received from the sun and moon under such different conditions. We can only say that these ratios are themselves utterly changed from what they are in the visible spectrum, where we all know that the solar light is something like five hundred thousand times moonlight. It is probable that the solar heat received in this part of the spectrum is less than five hundred times the lunar; but the actual ratio is only very roughly determinable by our present means.

By comparison with the "heat"-spectra given in a previous memoir, we may also note the fact that some of the wavelengths given from ice are identifiable in the solar spectrum, nor (in view of the now established facts that the ratios of the heat at different parts of the spectra of two unequally hot bodies are functions of the wave-length) need it surprise us that we have also found that this part of the spectrum of the sun is not incomparably hotter than the corresponding part

of the ice-spectrum.

It may be asked if we can, after all, feel sure of the character of such minute amounts of heat in the presence of the already described reflected and diffused heat from the upper spectrum, considering the possibility that something may go wrong in the elaborate arrangement of the sifting-train, and leave us (as everything we study now is invisible) without ocular warning of the fact. I may reply that we have lately found an admirable check upon the efficiency of our optical devices in the behaviour of that familiar substance lampblack, which all physicists use either on thermometers, thermopiles, or bolometers. All of us know probably that it is not absolutely non-selective, as it used to be thought, and that it has a tendency to transmit the infra-red with greater freedom than the visible spectrum; but the statement I am about to make may excite surprise. It is that when a very perfectly polished rock-salt plate is covered by a sheet of lampblack of such thickness as to transmit less than one per cent. of ordinary white light, it transmits about ninety per cent. of the radiations belonging to these extreme wave-lengths. In other words, it has become a transparent body to rays of this wave-length, while it exercises an intermediate degree of absorption on intermediate rays, so that by the amount of their absorption by lampblack we have a test by which these latter may be

independently identified.

We have given this study not only to map new lines and bands in the region between  $3^{\mu}$  and  $5^{\mu}$ , but also to verify the existence of an all but infinitesimal amount of heat at much greater wave-lengths. We have applied great pains to this latter, not so much on account of its own importance as on account of the important conclusions to be drawn from it later; for if it is true that in this extreme spectral region, corresponding to temperatures much below the boiling-point and even below that of melting ice, the amount of the solar heat is trivial, it is also true that the fact of its existing at all is of very significant interest to the meteorologist; for it is obviously here, at temperatures below 100° C., that the rays which make up the nocturnal as well as diurnal radiations from the soil of our own planet are to be found. We observe that if such rays can enter the air from the sun, they can go out even from an icy soil (and still more from an ordinary one), to whose radiations it hence appears the atmosphere is more or less permeable. Heat, then, apparently escapes in some very minute degree even from the surface of the Arctic regions, not only by convection but by direct radiation through the atmosphere towards space. Meteorological questions of great interest, to which we shall return in a later memoir, can best be answered from a study of this region; and even if the problem of the lunar temperature did not interest us as students of celestial physics, we should still find others

depending on it of very practical import.

As to the degree of accuracy obtainable in fixing its position. we may remind the reader that the old formulæ of Cauchy and others being useless, as we have shown, we have already undertaken a research \* to enable us to determine such wavelengths in this region. We have determined all the wavelengths by the interpolating curve made from the observations of this year, which has been exhibited to the Academy at its April meeting. In this memoir will be found all the explanations we can offer relating to the degree of trustworthiness of the values assigned to the present extreme wave-lengths. If they are, as we believe, to be trusted within the limits there given, we have measured indications of lunar heat (and possibly of solar) greater than are shown on this drawing, and whose wave-lengths exceed one fiftieth of a millimetre. It is not likely that the more refrangible of that extremely feeble heat, which we here particularly describe, is much less than 114.

I think we may now feel justified in saying that we probably know some of the main facts about the solar spectrum, so far as terrestrial absorption is concerned. Broadly speaking, they

are these :-

Hardly one fourth of the solar energy, as we get it, is visible, at least without special precautions. Of the remaining three fourths, by far the larger portion of the heat actually received lies in the region above 2<sup>\mu\_\*</sup>8, which has already been delineated, but if it were not for terrestrial absorption, the heat in the region below it might not improbably be relatively greater.

The effects of terrestrial absorption appear in the visible spectrum chiefly by means of the Fraunhofer lines, so that our first impression on looking at it is that these lines only occasionally interrupt the play of light and colour by which the solar energy makes itself known through the sense of vision. As we go down into those lower parts of the infra-red region, we find (directly contrary to the old belief) that, broadly speaking, the heat apparently grows more and more transmissible by our atmosphere, and this because the heat between the lines grows more and more transmissible, while the lines themselves, though growing into broader bands of almost total absorption, have not yet extinguished the hot regions

<sup>\* &</sup>quot;On hitherto unrecognized Wave-lengths," Phil. Mag. August 1886.

between them, so that, even taking regions of transmission and absorption together, on the whole here, *i.e.* above 3", more of dark heat in proportion is, perhaps, transmitted than

of light heat.

We may roughly illustrate\* this portion of the sun's spectrum after absorption by saying that, if it were visible, it would present almost the appearance of diffuse luminous bands on a dark field, somewhat like those seen in the spectra of stars of the fourth type. As we have observed that absorption seems to increase in the same direction in the sun's own atmosphere as in ours, it would be interesting to know if any thing analogous exists in the absolute solar spectrum, i.e. before absorption in the sun's atmosphere, but this we are not as yet able to determine.

as yet able to determine. Since in the part of t

Since, in the part of the spectrum described here for the first time, the same process of aggregation into ever wider and wider regions of absorption is continued till these intermediate regions of transmission disappear, the whole, to repeat an expression I have used in a earlier memoir, seems to become one continuous cold band, in which, however, we have found a little heat struggling through in the part beyond 11<sup>th</sup>. Briefly, then, we may say, that to an eye which could see the whole spectrum, visible and invisible, the luminous part being, as we know, interrupted by occasional dark lines, the lower part to 5<sup>th</sup> would appear to consist of alternate bright and dark bands, and the part below 5<sup>th</sup> be nearly dark, but with feeble "bright" bands at intervals.

In conclusion, we may say that these new researches extend the known solar spectrum from three to much over eighteen microns, shown on our plate, and while confirming the previously announced fact that the solar heat which reaches us here is negligible in amount, show from the fact of the existence of any at all, that the anomaly of our being able to perceive lunar heat where we could not formerly detect solar, can be explained consistently with the possible existence in

the latter of every wave-length before absorption.

These investigations into a problem of Solar Physics have also incidentally led us to the prospective means of solution of an important one in Meteorology, for they have opened to observation the hitherto unknown region of the spectrum in which the nocturnal and diurnal radiations, not only from the moon toward the earth, but from the soil of the earth toward space, are to be found and may be hereafter studied in detail.

LX. On the Application of Sir William Thomson's Theory of a Contractile Æther to Double Refraction, Dispersion, Metallic Reflexion, and other Optical Problems. By R. T. GLAZEBROOK, M.A., F.R.S.\*

IN any isotropic elastic solid there are, in general, two velocities of wave-propagation-one for normal waves, given by  $\sqrt{\Lambda/\rho}$  in Green's notation; the other, given by  $\sqrt{B/\rho}$ , for transverse waves; and when any system of waves falls on the bounding surface of two such media both these disturbances are set up. Since light-waves are entirely transverse, and do not give rise to normal waves possessing, at any rate, more than a very small fraction of the energy of the incident waves, it follows, as was shown by Green, that the ratio A/B is, for the æther, either extremely large or extremely small. If the surfaces of the solid at a finite distance from the origin be free, it is necessary, in order that the equilibrium position may be one of minimum potential energy, that A-4B should be positive, and hence Green supposed that A was very large and the æther incompressible. view has generally been accepted by English writers on

optical subjects.

In his paper "On the Reflexion and Refraction of Light," in the last number of this Magazine, Sir William Thomson, however, has shown that, "provided we suppose the medium to extend all through boundless space or give it a fixed containing vessel as its boundary," the conditions for stability in the æther are satisfied if we suppose that neither A nor B is negative. Under these circumstances it is not necessary that A should be greater than 4B, it is sufficient that A should be zero or positive. Such a medium, according to Sir William Thomson, is afforded us by homogeneous airless foam held from collapse by adhesion to a bounding vessel which may be infinitely distant all round, and for this medium A is zero, i. e. the medium is incapable of transmitting normal waves. On this hypothesis as to the nature of the æther it is possible to suppose that the absence of the normal wave is because A is zero, not because it is infinite. Sir William Thomson has, in in his paper just referred to, treated the problem of reflexion and refraction on this supposition; the object of the present communication is to consider double refraction and other allied

In my Report on Optical Theories, presented to the British Association at Aberdeen (B. A. Report, 1885, p. 179), when discussing the equations which are given by certain theories

<sup>\*</sup> Communicated by the Author.

of double refraction, I say:—"The question arises, Are these equations incompatible with Fresnel's wave-surface? Lord Rayleigh has of course proved that they are if the equation

$$\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} = 0,$$

expresses an absolutely necessary condition;" i.e. if the æther is incompressible, u, v, w being the displacements; "but it is not difficult to show that if, instead of the above equation, we put

 $\frac{1}{a^2} \frac{du}{dx} + \frac{1}{b^2} \frac{dv}{dy} + \frac{1}{c^2} \frac{dw}{dz} = 0$ 

(a, b, c being the principal wave-velocities), then the wave-surface will be Fresnel's, the direction of vibration will be normal to the ray, and will be in a plane containing the ray, the wave-normal, and an axis of the section of the ellipsoid  $a^2x^2 + b^2y^2 + c^2z^2 = 1$  by the wave-front, while the velocity of propagation will be inversely proportional to the length of this axis."

At the date at which this extract was written I believed that the æther must necessarily be incompressible, and therefore that the suggestion there made was impossible. The recent paper of Sir William Thomson's has shown that the condition of incompressibility is not necessary, and I propose, therefore, to develop the theory given in outline in the Report.

Before so doing I wish to refer to three points in Sir William Thomson's paper. He shows there that, under the conditions already stated, viz. no motion at infinity, the

expression

$$W = \frac{1}{2} \iiint dx \, dy \, dz \, \left[ A \left( \frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} \right)^{2} + B \left\{ \left( \frac{dw}{dy} + \frac{dv}{dz} \right)^{2} + \left( \frac{du}{dz} + \frac{dw}{dx} \right)^{2} + \left( \frac{dv}{dx} + \frac{du}{dy} \right)^{2} \right\}$$

$$-4B \left\{ \frac{dv}{dy} \frac{dw}{dz} + \frac{dw}{dz} \frac{du}{dx} + \frac{du}{dx} \frac{dv}{dy} \right\} \right], \quad . \quad . \quad (1)$$

which is Green's value for the work required to strain the solid, transforms into

$$\frac{1}{2} \iiint dx \, dy \, dz \left[ A \left( \frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} \right)^{2} + B \left\{ \left( \frac{dw}{dy} - \frac{dv}{dz} \right)^{2} + \left( \frac{du}{dz} - \frac{dw}{dx} \right)^{2} + \left( \frac{dv}{dx} - \frac{du}{dy} \right)^{2} \right\} \right], \quad (2)$$

and then, for the optical problem, A is put equal to zero. Now the term with B for a coefficient in this expression is

exactly the expression assumed by MacCullagh in his theory of reflexion, and which Stokes has shown (B. A. Report, 1862, p. 278) to be impossible as an expression for the energy of a strained solid, for it leads to the equations  $T_{xy} = -T_{yx}$ , &c., instead of  $T_{xy} = T_{yx}$ , where  $T_{xy}$  means the stress parallel to y on a plane normal to x; how, then, can it represent the

energy of the strained medium? The explanation of this point is simple. The second expression for W only gives the energy of the whole solid under certain surface-conditions. Each element of the integral is not an expression for the energy of the corresponding element of the solid; to find this we have to take into account the surface-integrals introduced by the transformation. These surface-integrals it is true vanish when the whole medium is considered; but in calculating the stresses on each element they are of importance, and when they are taken into account the true values are found for  $T_{xy}$  &c. We cannot get these values from the transformed expression directly, for that is only true under certain conditions.

A second point is the following:—The integral

$$\iiint \left(\frac{dv}{dy}\frac{dw}{dz} + \ldots\right) dx dy dz$$

is transformed into

$$\iiint \left(\frac{dv}{dz}\frac{dw}{dy} + \dots\right) dx \ dy \ dz$$

+ certain surface-integrals.

These surface-integrals vanish if u, v, w are all zero at the surface. They also vanish whenever u, v, w are functions of the same function of x, y, z and t. Thus, as I pointed out in a paper on the Reflexion and Refraction of Light (Proc. Camb. Phil. Soc. vol. iii. 1880), if W denote the true expression for the work W', the transformed expression W = W' + M, where M is a quantity which may be negative, but which vanishes if u, v, w are functions of the same function of the variables.

There remains the third point. Let us suppose that, in transforming, as is done by Sir William Thomson, the integral for W we pass across a surface at a finite distance from the origin, in crossing which the rigidity changes from B to B'. Unless either there is no motion over this surface, which is impossible, or certain relations hold in addition to the ordinary surface-conditions among the stresses, implying of course the existence of surface-tractions &c. other than those which arise from the strains, the surface-integral occurring in the transformation does not vanish, and the surface

contributes something to the energy. It follows, hence, that we must have the condition  $B\!=\!B'$  satisfied, and optical differences must arise from differences in the optical density of the æther on either side of the surface. In the paper this relation is assumed to simplify the formulæ, the foregoing considerations show that it is necessary. This point, however, is dealt with by Sir William Thomson himself in a note in this number of the Philosophical Magazine.

To turn now to the problem of Double Refraction. Since, according to our theory, the rigidity of the æther is the same in all media, it is clear that we cannot explain double refraction by variation of rigidity in different directions in a crystal, and we are driven to consider the hypothesis advanced by Rankine, Stokes, and Rayleigh, and which has been shown by the latter two to lead, if the æther be incompressible, to a

wave-surface other than that of Fresnel.

According to this hypothesis the density of the æther is to be treated as a function of the direction of displacement. The kinetic energy will be a quadratic function of the displacements, and for one set of axes may be written

$$\frac{1}{2} \iiint (\rho_x \dot{u}^2 + \rho_y \dot{v}^2 + \rho_z \dot{w}^2) \ dx \, dy \, dz.$$

We suppose that these axes coincide with the axes of the crystal. The potential energy has, according to our supposition, its usual form, and the constants A, B are the same as those for an isotropic medium. Thus, following Lord Rayleigh's paper (Phil. Mag. June 1871), we have as the equations of motion\*:—

$$\rho_{x} \frac{d^{2}u}{dt^{2}} = (A - B) \frac{d\delta}{dx} + B \nabla^{2}u$$

$$\rho_{y} \frac{d^{2}v}{dt^{2}} = (A - B) \frac{d\delta}{dy} + B \nabla^{2}v$$

$$\rho_{z} \frac{d^{2}w}{dt^{2}} = (A - B) \frac{d\delta}{dz} + B \nabla^{2}w$$

$$\delta = \frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} \cdot \dots \qquad (4)$$

where

Hence, differentiating with regard to x, y, z, and adding,

$$\frac{d^2}{dt^2} \left( \rho_x \frac{du}{dx} + \rho_y \frac{dv}{dy} + \rho_z \frac{dw}{dz} \right) = A \nabla^2 \delta. \qquad (5)$$

\* A theory leading to equations practically the same as these has been given by Sarrau, Liouville Journal, ser. ii. tomes xii. and xiii. (see Glazebrook, "Report on Optical Theories," B. A. Report, 1885, p. 174), and by Boussinesq, Liouville Journal, ser. ii. tome xiii. (Glazebrook, "Report on Optical Theories," p. 213), and in these the same conclusions as to the direction of vibration are arrived at.

Let  $lx + my + nz - \nabla t$  give the position of the wave-front at any instant. Let  $\lambda$ ,  $\mu$ ,  $\nu$ , be the direction-cosines of the displacement, and let O be the amount of the displacement. Then

$$u = \lambda \Theta, \quad v = \mu \Theta, \quad w = \nu \Theta,$$

and hence

$$\lambda \rho_x^{\gamma} \frac{d^2 \Theta}{dt^2} = (\mathbf{A} - \mathbf{B}) \frac{d}{dx} \left( \lambda \frac{d\Theta}{dx} + \mu \frac{d\Theta}{dy} + \nu \frac{d\Theta}{dz} \right) + \mathbf{B} \lambda \nabla^2 \Theta, \quad (6)$$

Now let

$$\Theta = \Theta_0 e^{\iota(lx + my + nz - \nabla t)}; \qquad . \qquad (7)$$

then

Substituting in the equations we find

$$\lambda \rho_x \nabla^2 = (\mathbf{A} - \mathbf{B}) l (l\lambda + m\mu + n\nu) + \mathbf{B}\lambda \mu \rho_y \nabla^2 = (\mathbf{A} - \mathbf{B}) m (l\lambda + m\mu + n\nu) + \mathbf{B}\mu \nu \rho_z \nabla^2 = (\mathbf{A} - \mathbf{B}) n (l\lambda + m\mu + n\nu) + \mathbf{B}\nu$$
(9)

$$V^{2}\{\rho_{x}l\lambda + \rho_{y}m\mu + \rho_{z}n\nu\} = A(l\lambda + m\mu + n\nu). \qquad (10)$$

Now put

$$a^2 = B/\rho_x$$
,  $b^2 = B/\rho_y$ ,  $c^2 = B/\rho_z$ .

Then

$$B\lambda \left(\frac{\nabla^{2}}{a^{2}}-1\right) = (A-B)l(l\lambda+m\mu+n\nu)$$

$$B\mu \left(\frac{\nabla^{2}}{l^{2}}-1\right) = (A-B)m(l\lambda+m\mu+n\nu)$$

$$B\nu \left(\frac{\nabla^{2}}{c^{2}}-1\right) = (A-B)n(l\lambda+m\mu+n\nu)$$
(11)

and

$$B\nabla^{2}\left\{\frac{l\lambda}{a^{2}}+\frac{m\mu}{b^{2}}+\frac{n\nu}{c^{2}}\right\}=A(l\lambda+m\mu+n\nu). \quad (12)$$

Multiply the first of equations (11) by l, divide by  $(\nabla^2 - a^2)$ , and so on, and add the three. Then we find

$$B\left(\frac{l\lambda}{a^{2}} + \frac{m\mu}{b^{2}} + \frac{n\nu}{c^{2}}\right)$$

$$= (A - B) (l\lambda + m\mu + n\nu) \left(\frac{l^{2}}{V^{2} - a^{2}} + \frac{m^{2}}{V^{2} - b^{2}} + \frac{n^{2}}{V^{2} - c^{2}}\right). \quad (13)$$

Hence, and from (12),

$$\frac{l^2}{V^2 - a^2} + \frac{m^2}{V^2 - b^2} + \frac{n^2}{V^2 - c^2} = \frac{A}{A - B} \frac{1}{V^2}.$$
 (14)

This is the general form of the equation of wave-slowness, without any assumption as to the relative magnitudes of A and B. If the æther be incompressible (Rankine, Stokes, 526

Rayleigh), A is infinite, and the right-hand side is  $1/V^2$ . If, on the other hand, A vanishes (Thomson), the right-hand side is zero, and the equation becomes

$$\frac{l^2}{V^2 - a^2} + \frac{m^2}{V^2 - b^2} + \frac{n^2}{V^2 - c^2} = 0. \quad . \quad . \quad (15)$$

which is Fresnel's surface.

To trace the form of the surface in general, let us find its section by the principal planes. Suppose a, b, c to be in order of magnitude, and let A/(A-B) = -k. Consider the section by the plane of zx. Then m=0, and we have

$$(\nabla^2 - b^2) [\nabla^2 \{ l^2 (\nabla^2 - c^2) + n^2 (\nabla^2 - a^2) \} + k(\nabla^2 - c^2) (\nabla^2 - a^2) ] = 0. (16)$$

Thus the section consists of a circle given by V=b, and the quartic curve

$$\nabla^{4}(1+k) - \nabla^{2}\{(l^{2}c^{2} + n^{2}a^{2}) + k(a^{2} + c^{2})\} + ka^{2}c^{2} = 0. \quad . \quad (17)$$

The two important cases are given by k=-1 (Rankine, Stokes, Rayleigh); and k very small, probably zero (Thomson). For the latter case, on solving the quadratic and neglecting  $k^2$  and higher powers, the two roots are

$$V_2^2 = a^2 n^2 + c^2 l^2 + \frac{k(a^2 - c^2)^2 l^2 n^2}{a^2 n^2 + c^2 l^2};$$
 (18)

and

$$V_3^2(1+k) = \frac{ka^2c^2}{a^2n^2+c^2l^2}.$$
 (19)

Thus the section of the surface of wave-slowness by this plane will be, for the nearly transverse waves, the circle given by

$$\frac{1}{r^2} = b^2;$$
 . . . . . (20)

and a curve differing from an ellipse by extremely small quantities depending on  $k(a^2-c^2)^2$ , and given by

$$\frac{1}{r^2} = a^2 n^2 + c^2 l^2 + \frac{k (a^2 - c^2)^2 l^2 n^2}{a^2 n^2 + c^2 l^2}; \qquad (21)$$

and for the condensational wave, the inverse of an ellipse, given by

$$\frac{1+k}{r^2} = \frac{ka^2c^2}{a^2n^2 + c^2l^2}.$$
 (22)

Moreover for the velocity of the condensational wave along the axis of x we find the value  $\sqrt{\frac{k}{1+k}}a$ . If we substitute

the values of a and k, this reduces to

$$\sqrt{A/\rho_s}$$
.

The three principal normal velocities then are:-

$$\sqrt{A/\rho_x}$$
,  $\sqrt{A/\rho_y}$ ,  $\sqrt{A/\rho_z}$ ;

while for the nearly transverse waves they are:-

$$\sqrt{B/\rho_x}$$
,  $\sqrt{B/\rho_y}$ ,  $\sqrt{B/\rho_z}$ .

The sole condition, therefore, for the disappearance of the normal wave is that A should be extremely small compared with B. This is the same as for an isotropic medium.

Taking, now, the extreme case in which A vanishes in comparison with B, let us determine the relations between the direction of vibration  $\lambda$ ,  $\mu$ ,  $\nu$ , and that of propagation l, m, n.

If we put A=0 in (5), we get

$$\rho_x \frac{du}{dx} + \rho_y \frac{dv}{dy} + \rho_z \frac{dw}{dz} = 0, \quad . \quad . \quad . \quad (23)$$

or

$$\frac{b\lambda}{a^2} + \frac{m\mu}{b^2} + \frac{n\nu}{c^2} = 0. \qquad (24)$$

Now if l, m, n are the direction-cosines of a normal to the ellipsoid,

 $a^2x^2 + b^2y^2 + c^2z^2 = 1$ , . . . (25)

then the direction-cosines of the line, joining the centre of the ellipsoid to the point of contact of the tangent-plane

$$lx + my + nz = 1$$
 . . . . (26)

are proportional to

$$l/a^2$$
,  $m/b^2$ ,  $n/c^2$ .

Hence  $\lambda$ ,  $\mu$ ,  $\nu$ , or the direction of vibration, lies in a plane normal to that radius vector of the ellipsoid (25) which is drawn to the point of contact of (26).

Again, from (9) we have

$$\nabla^2 - a^2 = \frac{\mathbf{A} - \mathbf{B}}{\mathbf{B}} (l\lambda + m\mu + n\nu) \frac{a^2 l}{\lambda}, \quad . \quad (27)$$

and two similar equations. Whence

$$b^{2}-a^{2} = \frac{A-B}{B} (l\lambda + m\mu + n\nu) \left( \frac{a^{2}l}{\lambda} - \frac{b^{2}m}{\mu} \right),$$

$$c^{2}-b^{2} = \frac{A-B}{B} (l\lambda + m\mu + n\nu) \left( \frac{b^{2}m}{\mu} - \frac{c^{2}n}{\nu} \right);$$
(28)

and from these,

$$\frac{a^2l}{\lambda}(b^2-c^2) + \frac{b^2m}{\mu}(c^2-a^2) + \frac{c^2n}{\nu}(a^2-b^2) = 0. \quad . \quad (29)$$

Thus, for all values of A and B, the line  $\lambda$ ,  $\mu$ ,  $\nu$  lies on the

cone given by (29), and this with equation (24) determines

its position completely.

Again, let x, y, z be the coordinates of the point in which the wave-front touches the wave-surface. Then we have\*, if  $x^2+y^2+z^2=r^2$ .

Also from (9) or (27), we find

$$\frac{\lambda}{a^2 l} = \frac{\mu}{b^2 m} = \frac{\nu}{c^2 n} = \kappa \text{ say.} \quad . \quad (32)$$

$$\frac{\lambda}{V^2 - a^2} = \frac{\nu}{V^2 - b^2} = \frac{\nu}{V^2 - c^2}$$

Thus

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$$\lambda = \kappa \left( \frac{V^2 l}{V^2 - a^2} - l \right).$$

Hence

$$(r^{2}-V^{2})\lambda = \kappa \left\{ V^{2} \frac{r^{2}-V^{2}}{V^{2}-a^{2}} l - l(r^{2}-V^{2}) \right\}$$

$$= \kappa \left\{ V^{2} \left( \frac{r^{2}-V^{2}}{V^{2}-a^{2}} + 1 \right) l - lr^{2} \right\}$$

$$= \kappa \left\{ xV - lr^{2} \right\} . \qquad (33)$$

Thus

Now x, y, z give the direction of the ray corresponding to the wave-normal l, m, n, and the direction of vibration  $\lambda, \mu, \nu$ . Thus the direction of vibration is normal to the ray.

Again, multiply (11) by  $\lambda/a^2$  &c. and add. Then

$$\frac{\lambda^{2}}{a^{2}} \left( \frac{V^{2}}{a^{2}} - 1 \right) + \frac{\mu^{2}}{b^{2}} \left( \frac{V^{2}}{b^{2}} - 1 \right) + \frac{\nu^{2}}{c^{2}} \left( \frac{V^{2}}{c^{2}} - 1 \right) 
= \frac{A - B}{B} \left( l\lambda + m\mu + n\nu \right) \left( \frac{l\lambda}{a^{2}} + \frac{m\mu}{b^{2}} + \frac{n\nu}{c^{2}} \right) 
= \frac{A(A - B)}{B^{2}V^{2}} \left( l\lambda + m\mu + n\nu \right)^{2} . . . . (35)$$

<sup>\*</sup> Aldis, 'Tract on Double Refraction,' page 12.

Take the case in which A=0, and let

$$\lambda' = \lambda/a^2$$
,  $\mu' = \mu/b^2$ ,  $\nu' = \nu/c^2$ .

Then (35), (24), and (29) become

$$l\lambda' + m\mu' + n\nu' = 0, \dots (37)$$

$$\frac{l}{\lambda'}(b^2-c^2) + \frac{m}{\mu'}(c^2-a^2) + \frac{n}{\nu'}(a^2-b^2) = 0. \quad . \quad (38)$$

Thus, draw a plane normal to the direction of vibration to touch the ellipsoid. The quantities  $\lambda'$ ,  $\mu'$ ,  $\nu'$  will be the direction-cosines of the radius vector to the point of contact, and

this radius vector, by (37), lies in the wave-front.

Moreover, the velocity of propagation is given by the length of the radius vector in the direction  $\lambda', \mu', \nu'$ ; and this radius vector is an axis of the section of the ellipsoid by the wavefront. This is, of course, Fresnel's construction for the velocity. If Fresnel's construction were completely fulfilled,  $\lambda', \mu', \nu'$  would give the direction of vibration. As it is, that direction is given by  $a^2\lambda'$ ,  $b^2\mu'$ ,  $c^2\nu'$ ; and these are the direction-cosines of the perpendicular on the tangent-plane to the ellipsoid at the point where it is met by  $\lambda', \mu', \nu'$ .

Moreover, this perpendicular clearly lies in the plane which contains the wave-normal, and the axis of the section of the ellipsoid by the wave-front; and since, according to Fresnel, the axis is the projection of the ray on the wave-front, the ray

lies in this same plane.

Thus, in fig. 1, let O N represent the wave normal and O R

Fig. 1.

the ray. Take a section of the ellipse  $a^2x^2 + b^2y^2 + c^2z^2 = 1$  by the plane NOR. Let OP be a radius of that section perpendicular to ON; OP is in the wave-front, and is the axis

of the section of the ellipsoid by the wave-front. According to Fresnel, OP is the direction of vibration in the ray OR. According to the theory of the present paper this is not the case.

Let PY be the tangent at P to the ellipse PNR, and OY perpendicular on PY. PY is the trace on the plane PNR of the tangent-plane to the ellipsoid; and this plane is perpendicular to the plane PNR, so that OX is the normal to the tangent-plane at P. According to our theory, OY is the direction of vibration, and moreover OY is perpendicular to OR.

Now experiment\* shows us that Fresnel's construction for the velocity is very closely indeed approached to; and hence A must be, if not actually zero, very small indeed. We have, however, no exact experimental evidence on the direction of vibration in a crystal; and it would be extremely difficult to devise an experiment which would decide between Fresnel's result and that of the theory now suggested. So far, then, as experimental evidence is concerned we may claim that the theory here given is in very close accordance with our present results. It has moreover the extreme advantage of basing the laws of double refraction on variations of the property of the æther, on which ordinary reflexion and refraction almost certainly depend.

Refraction occurs because the optical density of the æther is different in different media; double refraction, because in a crystal the optical density is different in different directions.

It remains now to consider what is meant by the optical density of the ether, and how it can vary in different media, or in different directions in the same medium. nomena of aberration and the other optical effects produced by the motion of transparent bodies are more easily explicable if we suppose the actual density of the æther as well as its rigidity to be the same in all bodies. Let us make this assumption for the present. Now the motion of the æther within a transparent body is not free; in addition to the forces arising from its own rigidity there must be others arising from the action of the transparent matter; and though we are ignorant of the nature of this action we can show, remembering that light-waves travel through the medium with a velocity which is independent of the amplitude, that the forces resolve themselves into two sets. One of these makes its appearance in such a way as to be equivalent to an increase in the density of the æther, while the other is

<sup>\*</sup> Stokes, Proc. Roy. Soc.; B. A. Report, 1862. Glazebrook, Phil. Trans. 1879, part i.; 1879, part ii. Hastings, Silliman's Journal.

equivalent to an increase in its rigidity. Thus, suppose we have a magnetized steel spring vibrating, by placing it in water we increase the effective inertia of the spring, but by placing it in a magnetic field we may stiffen the spring. To express the same in analytical terms the solution of our differential equation is to be, supposing we have a wave travelling parallel to the axis of z,

$$u = k \sin n (z - \nabla t)$$
.

And this is a solution of

$$\frac{d^{2}}{dt^{2}} \left\{ \rho + a + b \frac{d^{2}}{dz^{2}} + c \frac{d^{4}}{dz^{4}} + \dots \right\} u 
= B \frac{d^{2}}{dz^{2}} \left\{ 1 + a' \frac{d^{2}}{dz^{2}} + b' \frac{d^{4}}{dz^{4}} + \dots \right\} u,$$

 $\rho$  being the density of the æther in free space, B its rigidity, and a, b, a', b', &c. constants. These terms or some of them may give the action of the matter on the æther, those in a, b, c &c. enter the equations as an effective increase of density, those in a', b', &c. as an increase of rigidity.

To state the same fact in another way, the equations of motion of the either may be written

$$\rho \frac{d^2 u}{dt^2} = (\mathbf{A} - \mathbf{B}) \frac{d\delta}{dx} + \mathbf{B} \nabla^2 u + \mathbf{X}, \quad . \quad . \quad (39)$$

where X represents the action of the matter on the æther. X is to have such a form as will allow the propagation of waves without the absorption of energy and with a velocity independent of the amplitude. It must also give us the ordinary laws of reflexion and refraction, and we must be able to explain by simple hypotheses the laws of double refraction, dispersion, anomalous dispersion, and metallic reflexion. Of late years a number of attempts have been made to find an expression for this quantity X. An account of them is given in my Report on Optical Theories (B. A. Report 1885). The most complete in some respects is that of Voigt, who, starting with the question as to what is the most general form consistent with the conditions imposed by the problem, comes to the conclusion that for an isotropic medium we may put

$$\mathbf{X} = -r \frac{d^2(u - \mathbf{U})}{dt^2} + a \frac{d^2(u - \mathbf{U})}{dz^2} + a' \frac{d^4(u - \mathbf{U})}{dz^2dt^2} - n(u - \mathbf{U}), (40)$$

where U is the displacement of the matter particles in the same element of volume as the æther, which has u, v, w for its component displacements. In a crystal other terms come in and the coefficients of these may be functions of the

The formulæ obtained by taking only the term -n(u-U) have been discussed at length by Von Helmholtz\* and Sir W. Thomson +.

Sir W. Thomson has shown that while the theory will account for dispersion it fails when we come to double refrac-

tion, for it makes that depend on the period ‡.

The first term  $-r\frac{d^2}{dt^2}$  (u-U) leads to equations for an isotropic medium which are practically identical with those employed by Ketteler. In fact he first suggested its use§.

He dismisses it shortly afterwards for reasons which do not seem to me to have great weight. The point is discussed in the Report on Optical Theories, p. 229. The theory leads to an account of dispersion which certainly agrees closely with experiment, and it will, as we shall see, explain double refraction satisfactorily, if we may assume Sir W. Thomson's theory of a contractile either. For if we write  $\rho'$  for r in Ketteler's expression and  $\rho_0$  for the density in free space, the equations of motion become

$$\rho_0 \frac{d^2 u}{dt^2} = (A - B) \frac{d\delta}{dx} + B \nabla^2 u - \rho' \frac{d^2}{dt^2} (u - U). \quad . \quad (41)$$

Now in a transparent medium in which there is no absorption, the value of U will be indefinitely small compared with that of u, and omitting it from the equation we get

$$(\rho_0 + \rho') \frac{d^2 u}{dt^2} = (\mathbf{A} - \mathbf{B}) \frac{d\delta}{dx} + \mathbf{B} \nabla^2 u. \qquad (42)$$

This is the equation which we have been dealing with all along. In a crystal the resistance offered to the motion of the æther will depend on the direction, and  $\rho'$  will have different values for the three axes. We then get

$$\rho_x \frac{d^2 u}{dt^2} = (\mathbf{A} - \mathbf{B}) \frac{d\delta}{dx} + \mathbf{B} \nabla^2 u, \quad . \quad . \quad . \quad (43)$$
&c.,

and these are the equations for a crystal.

The assumption, therefore, that the mutual reaction depends on the relative accelerations of matter and æther gives us formulæ which explain double refraction. To explain dis-

† Thomson, Baltimore Lectures. According to an account given recently in 'Nature' of the work of Prof. Lindemann on this subject, 'Nature,' August 23, 1888, he has surmounted this difficulty.

§ "Optische Controversen," Wied. Ann. t. xviii. p. 397, "Eine Dritte

Annahme."

<sup>\*</sup> Helmholtz, Pogg. Ann. t. cliv. p. 582.

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persion we adopt the view due originally to Sellmeier\* and developed lately by Sir W. Thomson in the Baltimore lectures. According to this view it arises from the absorption of some of the light energy by the molecules of the body, owing to the fact that the period of the light-waves nearly synchronizes with that of the natural vibrations of the molecules. The term in U in our equation becomes appreci-Of course in this case we need another equation to determine the motion of the matter molecules. The forces retarding this matter motion will arise partly from the reaction of the æther and partly from that of the matter itself. As to the expression for the latter we do not know what it is, but in order that the linear wave may be propagated it must depend on U and its differential coefficients. Let us suppose, taking the case of a plane wave travelling parallel to the axis of z, that the force is represented, as is assumed by Helmholtz, by

$$-\alpha^2 \mathbf{U} - \gamma^2 \frac{d\mathbf{U}}{dt}$$
.

If differential coefficients of U with respect to z do come in, we can allow for them by supposing  $\alpha^2$  and  $\gamma^2$  to be complex-operators. Such a supposition will alter the form of the

expression for  $\mu^2$ .

Now let us consider the æther and matter in a certain element of volume dv. Let  $\rho_0$  be the density of the æther, and let us further suppose, for the present, that a portion only of the matter molecules in the element are disturbed; we shall have to deal with the average displacements of these matter molecules; let them be U, V, W, parallel to the axis; and let  $\rho_1 dv$  denote the mass of matter within the element which is set in motion. If the whole of the matter in the element moves,  $\rho_1$  will be the density of the matter; in general we may suppose it to be less than the matter density and to depend on the number of matter molecules set in motion by the light-waves.

Hence the equations become,

$$\rho_{0} \frac{d^{2}u}{dt^{2}} + \rho' \frac{d^{2}}{dt^{2}} (u - U) = (A - B) \frac{d\delta}{dx} + B \nabla^{2}u$$

$$\rho_{1} \frac{d^{2}U}{dt^{2}} - \rho' \frac{d^{2}}{dt^{2}} (u - U) = -\alpha^{2}U - \gamma^{2} \frac{dU}{dt}$$
(44)

Thus putting  $\rho_0 + \rho' = \rho$ ,  $\rho_1 + \rho' = \rho_2$ , so that  $\rho$  is the effective density of æther when loaded by the matter,  $\rho_2$  the effective density of matter when loaded by æther, we have:—

\* Sellmeier, Pogg. Ann. t. cxlv. pp. 399, 520; t. cxlvii. pp. 386, 525. Phil. Mag. S. 5. Vol. 26. No. 163. Dec. 1888. 2 O

$$\rho \frac{d^{2}u}{dt^{2}} - \rho' \frac{d^{2}U}{dt^{2}} = (A - B) \frac{d\delta}{dx} + B \nabla^{2}u$$

$$\rho_{2} \frac{d^{2}U}{dt^{2}} - \rho' \frac{d^{2}u}{dt^{2}} = -\alpha^{2}U - \gamma^{2} \frac{dU}{dt}$$

$$(45)$$

The solution of equations practically the same as these has been given by Ketteler\*. It will be useful to have it here for the sake of completeness, and also because the notation is different.

Let the solutions be given by

Then, on substituting, we have

Then, on substituting, we have
$$u_0 \left\{ n^2 \left( \rho - \frac{\mathrm{B}}{\mathrm{V}^2} \right) - \mathrm{B} \left( \frac{2 \iota n k}{\mathrm{V}} - k^2 \right) \right\} = \mathrm{U}_0 n^2 \rho',$$

$$\mathrm{U}_0 \{ n^2 \rho_2 - \alpha^2 + \gamma^2 \iota n \} = u_0 n^2 \rho'.$$
(47)

Thus

$$\left\{ e^{2} \left( \rho - \frac{B}{V^{2}} \right) - B \left( \frac{2 \iota n h}{V} - k^{2} \right) \right\} \left\{ n^{2} \rho_{2} - \alpha^{2} + \gamma^{2} \iota n \right\} = n^{4} \rho'^{2}; (48)$$

$$\therefore \left\{ n^{2} \left( \rho - \frac{B}{V^{2}} \right) + Bk^{2} \right\} (n^{2} \rho_{2} - \alpha^{2}) + \frac{2B \gamma^{2} n^{2} k}{V} = n^{4} \rho^{2}; \quad (49)$$

$$\gamma^2 \left\{ n^2 \left( \rho - \frac{B}{V^2} \right) + Bk^2 \right\} - \frac{2Bk}{V} \left( n^2 \rho_2 - \alpha^2 \right) = 0 .$$
 (50)

and 
$$\frac{2Bk}{\nabla \gamma^2} \{ (n^2 \rho_2 - \alpha^2)^2 + n^2 \gamma^4 \} = n^4 \rho^{12}$$
. . . . . . . (52)

Thus 
$$\frac{2k}{n\nabla} = \frac{\gamma^2 \rho'^2 n^3}{\left[ \left\{ n^2 \rho_2 - \mathbf{x}^2 \right\}^2 + \gamma^4 n^2 \right] \mathbf{B}} . . . . . . (53)$$

$$\frac{1}{V^2} - \frac{k^2}{n^2} = \frac{\rho}{B} - \frac{\rho'^2 n^2 (n^2 \rho_2 - \alpha^2)}{\left[ (n^2 \rho_2 - \alpha^2)^2 + n^2 \gamma^4 \right] B} \quad . \quad . \quad (54)$$

Let

Let 
$$\alpha^2 = \nu^2 \rho_2$$
.  
Then  $\frac{2\bar{k}}{nV} = \frac{\gamma^2 \rho'^2 n^3}{[\rho_2(n^2 - \nu^2) + \gamma^4 n^2]B}$ . (55)

$$\frac{1}{V^2} - \frac{k^2}{n^2} = \frac{\rho}{B} - \frac{\rho'^2 \rho_2 n^2 (n^2 - \nu^2)}{[\rho_2^2 (n^2 - \nu^2)^2 + \gamma^4 n^2]B} \quad . \quad (56)$$

\* Ketteler, Theoretische Optik, § 42, and various papers alrady re-

† The symbols  $k, n, \lambda, \mu, \nu$ , have no longer the same signification as above, pp. 524 seq.

Also we find

$$\frac{U_0}{u_0} = \frac{n^2 \rho'}{\rho_2 (n^2 - \nu^2) + \gamma^2 \iota n} = Re^{-\iota \theta}, \qquad (57)$$

where

$$\left. \begin{array}{l}
R^{2} = \frac{n^{4} \rho^{12}}{(n^{2} - \nu^{2})^{2} \rho_{2}^{2} + \gamma^{4} n^{2}} \\
\tan \theta = \frac{\gamma^{2} n}{(n^{2} - \nu^{2}) \rho_{2}} \end{array} \right\}. \quad (58)$$

and

Now we notice that k is a quantity which depends on  $\gamma^2$  and is small therefore when  $\gamma^2$  is small. In a transparent body k must be practically zero, and hence we infer that for a transparent body  $\gamma^2$  is extremely small. The only reason for retaining the term at all lies in the fact that if we put  $\gamma^2=0$ , then for the value  $n^2=\nu^2$  we have the ratio  $U_0/u_0$  infinite.

Taking, then, a case in which  $\gamma^2$  is zero, and remembering that our solution fails for the critical value  $\nu^2$  of  $n^2$ , we have in general  $U_0/u_0$  small, and

$$\frac{1}{V^2} = \frac{\rho}{B} - \frac{\rho'^2 n^2}{B\rho_2(n^2 - \nu^2)}. \qquad (59)$$

Now let  $V_0$  be the velocity in vacuo of light of the frequency n;  $\lambda$  its wave-length.

Then

$$n=\frac{2\pi V_0}{\lambda}.$$

Put

$$\nu = \frac{2\pi V_0}{\lambda_1},$$

and substitute in (59)

$$\frac{1}{V^2} = \frac{\rho}{B} + \frac{\rho'^2}{B\rho_2} \frac{\lambda_1^2}{\lambda^2 - \lambda_1^2}. \quad . \quad . \quad . \quad . \quad (60)$$

Also, if  $\mu = V_0/V = \text{the refractive index.}$  Since  $V_0^2 = B/\rho_0$ ,

$$\mu^{2} = \frac{\rho}{\rho_{0}} + \frac{\rho^{\prime 2}}{\rho_{0}\rho_{2}} \frac{\lambda_{1}^{2}}{\lambda^{2} - \lambda_{1}^{2}} \cdot \cdot \cdot \cdot \cdot (61)$$

The quantity  $\rho/\rho_0$  is the square of the refractive index for waves of infinite length; put it  $\mu_{\infty}^2$ , and write C for  $\rho'^2/\rho_0\rho_2$ . Then

$$\mu^{2} = \mu_{\infty}^{2} + \frac{C\lambda_{1}^{2}}{\lambda^{2} - \lambda_{1}^{2}} \cdot \cdot \cdot \cdot \cdot (62)$$

This is Ketteler's dispersion formula, which he has proved agrees well with the results of experiment over a long range of values of  $\lambda^*$ .

By supposing, as is done by Sir W. Thomson in the Balti-\* Ketteler, Wied. Ann. xii. pp. 363, 481, xv. p. 336, and elsewhere. more Lectures, that there are a number of possible periods of motion for the matter particles corresponding to a series of values for  $\nu^2$  or  $\lambda_1^2$ , we get a series of terms in the expression for  $\mu^2$ , which becomes

 $\mu^{2} = \mu_{\infty}^{2} + \frac{C\lambda_{1}^{2}}{\lambda^{2} - \lambda_{1}^{2}} + \frac{D\lambda_{2}^{2}}{\lambda^{2} - \lambda_{2}^{2}} +$ 

Ketteler has shown that for Iceland spar, taking Mascart's measurements of refractive index, the above formula with three terms agrees very closely with experiment from

$$\lambda = .76013$$
 to  $\lambda = .31775$ .

The greatest difference is 0001 in the value of the refractive index.

This last formula may be transformed to a more useful form if we suppose  $\lambda_1$  is large compared with  $\lambda$ , so that we may neglect  $(\lambda/\lambda_1)^4$  and higher powers. We get then

$$\mu^{2} = \mu_{\infty}^{2} - C\left(1 - \frac{\lambda^{2}}{\lambda_{1}^{2}}\right)^{-1} + \frac{D\lambda_{2}^{2}}{\lambda^{2} - \lambda_{2}^{2}}$$

$$= \mu_{\infty}^{2} - C - \frac{C}{\lambda_{1}^{2}}\lambda^{2} + \frac{D\lambda_{2}^{2}}{\lambda^{2} - \lambda_{2}^{2}}$$

$$= a^{2} - k^{2}\lambda^{2} + \frac{D\lambda_{2}^{2}}{\lambda^{2} - \lambda_{2}^{2}} \cdot \dots \cdot (64)$$

Again, according to Ketteler \* this formula will give the dispersion in quartz with considerable accuracy from  $\lambda = 2.14$ to  $\lambda = 18$ , or through about 12 octaves; while it agrees very fairly with Langley's + observations for flint glass from

$$\lambda = 2.356$$
 to  $\lambda = .3440$ .

For flint glass the values for the constants given by Ketteler are

$$k^2 = .009076$$
 D=.60714  
 $a^2 = 2.44137$   $\lambda_2 = .029929$ 

According to the dispersion formula given above, the value of  $\mu^2$  is infinite for  $\lambda = \lambda_1$  or  $\lambda = \lambda_2$ . For these values the light will be absorbed in the medium. Moreover, for values of  $\lambda$  somewhat greater than  $\lambda_1$ ,  $\mu^2$  becomes a real negative quantity, and the light ceases to be transmitted. Now the characteristic property of substances which show metallic refraction is, according to Jamin and Quincke  $\ddagger$ , that  $\mu^2$  is a real negative quantity.

Thus the theory will explain ordinary metallic reflexion by

\* Ketteler, Wied. Ann. xxx. p. 312.
† Langley, "Professional Papers of the Signal Service," No. xv. A
Report of the Mount Whitney Expedition, p. 226.
† See Hon. J. W. Strutt [Lord Rayleigh], "Reflexion of Light from
Intensely Opaque Matter." Phil. Mag. 1872.

the supposition that  $\lambda_1$  is less than the wave-length of any part of the visible spectrum. Now  $\lambda_1$  is the wave-length corresponding to the free periods of the matter vibrations. Thus the free periods for the matter vibrations are less than those for any visible light. The application of the theory to thin metallic films, and to the small prisms investigated by Kundt, requires further consideration, and must be left for the present.

If this explanation be true, then a substance which is opaque to light might be transparent to waves of greater length, all that is required is that the length of such waves should be greater than the critical length  $\lambda_1$ . Professor J. J. Thomson has recently found this to be the case for ebonite, which transmits easily the long waves of electric disturbance in experi-Thus somewhere between ments such as those of Hertz. these electric vibrations and those of light, ebonite has a band of strong absorption, and, moreover, there are no free periods possible for the free-matter vibrations in ebonite, which are

less than the periods of the other vibrations.

Thus, to explain the effect of a metallic medium there is no need to invoke the aid of the terms in  $\gamma^2$  in the equations of Part of the effect may, it is true, be due to the existence of such terms; it is sufficient, however, that  $\lambda_1$  should be somewhat greater than  $\lambda$ , then  $\mu^2$  will, for some values of  $\lambda$ , be less than unity, and for others a real negative quantity. The appendix to Sir W. Thomson's Baltimore Lectures contains a discussion of this point, and the formulæ there given become those of the theory now considered if we write for C<sub>1</sub> &c. in Thomson's equation  $-4\pi^2C_1/\tau^2$ . (See 'Report on Double Refraction, p. 245 et seq.)

The theory will, without serious modification, give us the formula originally due to Fresnel and now fully verified by the experiments of Fizeau and Michelson, connecting the velocity of light in a moving medium with the velocity of the medium.

For suppose that the æther is at rest, and that a transparent body is moving through it with velocities L, M, N, parallel to Then in estimating the relative accelerations of the æther and the matter at a point fixed in the body, we must

remember that the value of  $\frac{d}{dt}$  will be

$$\frac{d}{dt} + \mathbf{L}\frac{d}{dx} + \mathbf{M}\frac{d}{dy} + \mathbf{N}\frac{d}{dz}.$$

So that taking the case of motion in the direction of propagation, the term  $\rho' \frac{d^2u}{dt^2}$  becomes  $\rho' \left(\frac{d}{dt} + N \frac{d}{dz}\right)^2 u$ ; and this, if we neglect N2 as small compared with the other quantities, gives us as the equation of motion,

$$\rho \frac{d^2 u}{dt^2} + 2N\rho' \frac{d^2 u}{dzdt} = B \frac{d^2 u}{dz^2}. \quad . \quad . \quad (65)$$

Hence if  $u = u_0 \sin \frac{2\pi}{\lambda} (z - \nabla t)$ ,

 $\rho \mathbf{V}^2 - 2\mathbf{N}\rho'\mathbf{V} - \mathbf{B} = 0.$ 

Hence

$$V = \frac{N\rho' + \sqrt{N^2\rho'^2 + B^2}}{\rho} = \frac{B + N\rho'}{\rho}.$$

$$\therefore V = V_0 + \frac{N\rho'}{\rho}, \quad . \quad . \quad . \quad (66)$$

to the same approximation, if V<sub>0</sub> is the velocity when the medium is at rest.

Again,  

$$\mu^{2} = \frac{\rho}{\rho_{0}} = \frac{\rho_{0} + \rho'}{\rho_{0}},$$

$$\therefore \frac{\rho'}{\rho_{0}} = \mu^{2} - 1;$$

$$\frac{\rho'}{\rho} = \frac{\mu^{2} - 1}{\mu^{2}},$$

$$\therefore \nabla = \nabla_{0} + \frac{\mu^{2} - 1}{\mu^{2}} N. \qquad (67)$$

and

And this is Fresnel's formula, which has been obtained by Boussinesq in a similar manner.

The consideration of phenomena connected with the rotation of the plane of polarization must be deferred to a future article.

It remains now to refer to one point of great importance which the theory as it stands will not explain.

Experiment shows us that in the case of the reflexion of light from transparent media Fresnel's tangent-formula does not hold. Some light is reflected near the polarizing angle. According to the theory the tangent-law is true at least when

Now it is clearly true that there must be a thin layer of the æther near the separating surface of two media, air and glass say, across which the optical density of the æther changes from that of air to that of glass. If this layer be infinitely thin compared with the wave-length, then the transition is practically sudden; but if the layer has a thickness comparable with the wave-length, then effects such as are actually observed would occur. And L. Lorenz \* has shown that the effects of elliptic polarization observed by Jamin would agree numerically with the results of a theory of gradual transition, if the thickness of the variable film lies between  $\frac{1}{10}$  and  $\frac{1}{100}$ of a wave-length.

<sup>\*</sup> Pogg. Ann. t. cxiv. p. 238; Glazebrook, Report on Optics, p. 188.

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To this explanation the objection \* has been made that the phenomena resemble those shown by thin films, and that the reflected light ought to be coloured. We may reply to this that the film is comparable with the thickness of the black film in Newton's rings, so that the colour shown, if any, would be that of the blue of the first order, and would probably —the light being very faint—hardly be noticed as colour by an observer who was not specially directing his attention to that point. I hope, however, shortly to investigate this question by direct experiment. Such observations of a preliminary character as I have made have shown a bluish tint in the reflected light. Moreover, if this light appear blue, so, too, ought the light which is reflected in considerable quantity from the black spot in a soap-film. fact, if we take Reinold and Rücker's value for the thickness of the black spot in a soap-film, the quantity of light reflected from it is much greater than that observed by Jamin near the polarizing-angle. For, taking the case of normal incidence, we have for the intensity of the reflected light in terms of the incident the value

$$I = \frac{4\left(\frac{\mu - 1}{\mu + 1}\right)^2 \frac{4\pi^2 D^2}{\lambda^2}}{\left\{1 - \left(\frac{\mu - 1}{\mu + 1}\right)^2\right\}^2}.$$

If we put  $\mu = \frac{4}{3}$ ,

$$\frac{\mu-1}{\mu+1}=\frac{1}{7}.$$

Then, approximately,  $1 = \frac{16\pi^2}{49} \times \frac{D^2}{\lambda^2} = \frac{10}{3} \frac{D^2}{\lambda^2}$ .

Now, according to Reinold and Rücker,

D=
$$\frac{1}{50}$$
λ;  
∴ I= $\frac{10}{3 \times 2500}$ =:0013.

Thus over one thousandth part of the incident light ought theoretically to be reflected, and the colour of this ought to be mixed in the inverse ratio of the square of the wave-lengths. I am not aware that any careful photometric observations on this light have been made; at any rate it is, I think, nowhere stated that it shows colour.

Now as to the Jamin effect †, we have

$$I = M^2 \tan^2(\phi - \phi')$$

<sup>\*</sup> Hon. J. W. Strutt [Lord Rayleigh], "On the Reflexion of Light from Transparent Matter," Phil. Mag. 1871.

<sup>†</sup> Jamin, Annales de Chimie et de Physique, 3 sér. t. xxix. Cours de Physique, iii. p. 525.

at the polarizing-angle, and, in Jamin's notation,  $M = \epsilon \sin \phi$ .

According to his observations for flint glass,  $\epsilon = 017$ ,  $\phi = 59^{\circ}.44$ .

Whence I = 000069.

If we take Quincke's \* observations, we find, from his table for reflexion at the surface of flint glass, the value I = 000096. Thus the value of I for glass is less than '0001, or one terth the amount of light that is reflected from the black film of a soap-bubble. Hence the light reflected from the bubble being brighter ought to show more colour than the light reflected from glass near the polarizing-angle.

Two explanations may be given of the fact that colour has not been noticed—except, possibly, in the rough observation of my own already referred to—in either case. The one is that, owing to its faintness, it has escaped the notice of observers who were not specially looking for it; the other lies in the fact that there seems some reason to suppose that our eyes are sensitive to light before they appreciate distinctions of colour. Either of these would, I think, be sufficient to account for the facts, and would allow us to believe that the explanation of the Jamin-effect given by Lorenz is the true one, though possibly further experiments, which I hope shortly to undertake, may be necessary to prove this. elliptic polarization depends greatly, it is true, as Wernicke † has shown lately, on the nature of the surface and of the means taken to polish it; but he comes to the conclusion "that it is a general property of bodies modified by the presence of a surface-film, but not entirely explained by that."

This surface-film of Wernicke's is, however, quite different from the surface-layer of æther of variable density considered by Lorenz. Wernicke's film is caused by the presence of foreign matter; the layer of varying density is necessary to the transition from air to glass, and it is only a question of how thick this layer is in comparison with the wave-length.

We conclude, then, that the theory here put forward accounts satisfactorily for reflexion and refraction both by transparent bodies and by metals, also for double refraction and dispersion, including the anomalous dispersion of such substances as cyanin, fuchsin, or the other anilin dyes, while it leads, in addition, to the correct expression for the velocity of light in a moving medium. As already stated, I hope to treat, in another paper, the consideration of the properties of quartz, the rotation produced by sugar, and the rotation in a magnetic field.

<sup>\* &</sup>quot;Optische Experimental Untersuchungen," Pogg. Ann. Band 127, 128, &c. † Wied. Ann. xxx. p. 468.

## LXI. Intelligence and Miscellaneous Articles.

COMPRESSIBILITY OF THE GASES OXYGEN, HYDROGEN, NITROGEN, AND AIR UP TO 3000 ATMOSPHERES. BY M. E. H. AMAGAT.

I HAVE followed the method which I have already used for studying liquids within the same limits of pressure, but the difficulty is here far greater; it arises more especially from the smallness of the volume which a gas occupies when it is somewhat powerfully compressed. After numerous trials, I have arrived at perfectly regular and concordant results by using for gauging the platinum-wire tubes the method of reading by electrical contacts, which then served to estimate in the same tubes the volumes successively occupied by the compressed gas.

I thus obtained for the same gas with different tubes graphical

traces which are almost absolutely coincident.

The results which I give further on, and which are merely apparent results, differ materially (numerically) from those at which Natterer arrived. The differences, which are somewhat irregularly distributed amount to several hundredths of atmospheres in the part common to our researches; for the same reduction in the volume of gas I find in general pressures far higher than those given by Natterer: this difference can be easily accounted for if we discuss the probable and even inevitable errors inherent in the method pursued by this physicist. The following results refer solely to high pressures; pressures below 1000 atmospheres will be investigated by an apparatus which enables me to raise the temperature far higher than I have been able with very high pressures, where I could only work between 0° and 50°.

The following table gives for the pressures specified in the first column the volumes occupied at 15°, by unit masses of gas, at the

same temperature and under the same pressure, 76 centim.

Atmospheres.	Air.	Nitrogen.	Oxygen.	Hydrogen.
750 1000 1500 2000 2500 3000	0·002200 0·001974 0·001709 0·001566 0·001469 0·001401	0·002262 0·002032 0·001763 0·001613 0·001515 0·001446	0·001735 0·001492 0·001373 0·001294 0·001235	0·001688 0·001344 0·001161 0·001047 0·000964

It is interesting to compare the compressibilities of strongly compressed gases among each other and with liquids. In order to facilitate this comparison I have calculated from 500 atm. to 800 atm. their coefficient of compressibility as usually defined with liquids. The following is the table of results obtained:—

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	ts of pratmosp			Air.	Nitrogen.	Oxygen.	Hydrogen.
Between	750 1000 1500 2000 2500	and ,, ,,	1000 1500 2000 2500 3000	0·000411 0·000268 0·000167 0·000123 0·000093	0·000407 0·000265 0·000170 0·000122 0·000091	0·000258 0·000160 0·000115 0·000091	0·000408 0·000272 0·000197 0·000158

It will thus be seen that at very high pressures oxygen, nitrogen, and air have almost the same compressibility; it is of the same order of magnitude as that of liquids; at 3000 atm., it is virtually equal to that of alcohol under the normal pressure.

The compressibility of hydrogen is far greater, almost double; at 3000 atm., it is almost equal to that of ether towards the normal

pressure.

It is easy to foresee that these compressibilities, like those of liquids, should increase with the temperature; that is shown by the following table with respect to hydrogen.

Limits of pressures		Coefficients.	
in atmospheres.	At 0°.	At 15°.4.	At 47°·3.
Between 1000 and 1500 ,, 1500 ,, 2000 ,, 2000 ,, 2500 ,, 2500 ,, 3000	0·000 0·000263 0·000196 0·000156	0·000408 0·000272 0·000197 0·000158	0·000416 0·000280 0·000208 0·000158

The apparent densities are easily deduced from the former table; assuming provisionally the number generally adopted for the compressibility of glass, the following results are obtained at 3000 atm.

Densities at 3000 atm. compared with water.

*	Apparent.	Real.
Oxygen	1.0972	1.1054
Air	0.8752	0.8817
Nitrogen	0.8231	0.8293
Hydrogen	0.0880	0.0887

The curves obtained, as I have already done, by putting the pressures on the axis of the abscisse, and the products pv on that of the ordinates, are nearly straight lines, but presenting all a slight concavity turned towards the axis of the abscisse; I shall return to this important point in reference to limiting volumes, when I have determined the alteration in volume of the envelopes.—Compte rendus, Sept. 17, 1888.

## OBSERVATIONS ON BREWSTER'S NEUTRAL POINT. BY MM. J. L. SORET AND C. SORET.

The neutral point of atmospheric polarization which is below the sun, and which was discovered by Brewster, has been rarely seen and determined, to judge at any rate from the publications on this subject. We have had occasion to observe it on the summit of the Righi (height 1800 metres) on the mornings of September 23 and 24, the height of the sun over the horizon being from 20° to 35°.

On the 23rd, from 8 to 9.40 a.m., in remarkably fine weather, it was easy to observe, by means of a Savart's polariscope, that in the immediate neighbourhood of the sun, above as well as below, the polarization of light was negative; that is to say, that the plane of polarization was perpendicular to the sun's azimuth. Below the sun the fringes of the polariscope gradually diminished in intensity, and disappeared at about 14° of angular distance; a little lower, inverse fringes were seen, the visibility of which increased to the horizon. In order not to be dazzled we interposed an opaque screen in front of the sun, or we placed ourselves in the shade of the iron column of the balcony.

Next day the sky was less clear; we have, however, been able

to repeat our observations.

The angular distance of the neutral point is difficult to measure owing to the feebleness of the polarization. We have taken it by determining by a sextant the height of the sun above the apparent horizon, formed by distant mountains; then measuring the distance of the neutral point from the horizon by a special apparatus sufficiently accurate to give angles to within 10'; the middle of the neutral space was sighted, which occupied about 4°.

The 24th September, by the aid of this latter apparatus, we have also determined simultaneously the distance of the neutral point

above the sun (Babinet's neutral point).

The following are the numbers which we have obtained:—

1888.	Berne Time.	Distance of the neutral point from the Sun.		
		Brewster.	Babinet.	
September 23  ", ", ", ", ", 24 ", "	h m 8 5 8 17 8 25 8 32 9 40 8 5 8 12 8 15 8 25	15 to 16° 17° 10 17° 20' 16 20' * 15° (about) 16 13° 16° 40' 15° 48'	15° 16° 15 to 16° 15 to 16°	

These measurements for the distance of Brewster's neutral point from the sun give very high numbers compared with those which Brewster himself † and M. F. Busch ‡ found. Is this a consequence of the altitude at which the observations are made? It would be premature to assert this.—Comptes rendus, October 15, 1888.

\* Measured directly with the sextant.

† Transactions of the Royal Society of Edinburgh, vol. xxiii., 1861.

1 Meteorological Zeitschrift for 1886.

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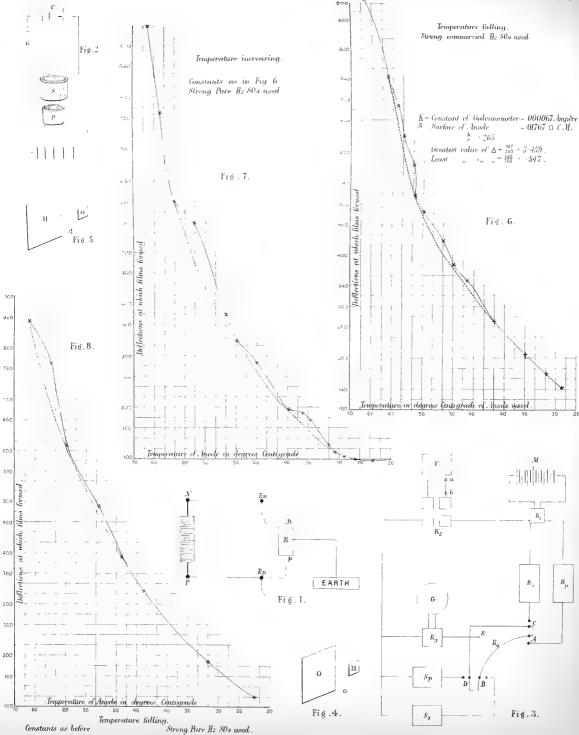
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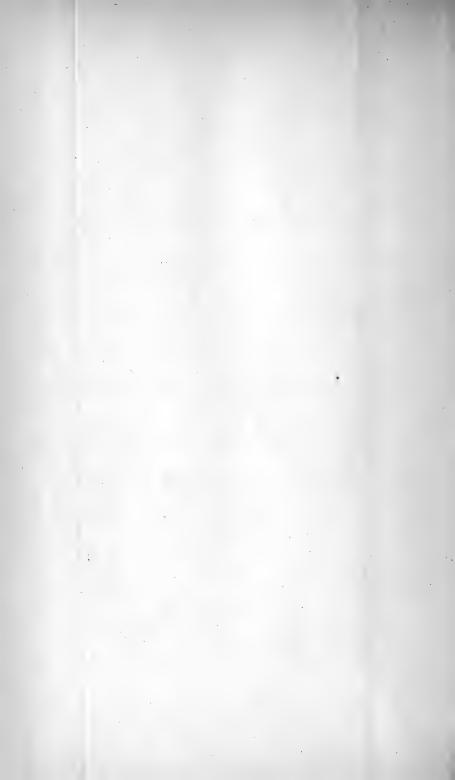
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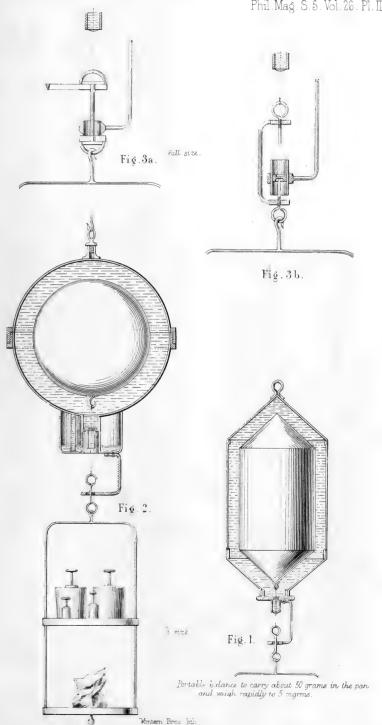
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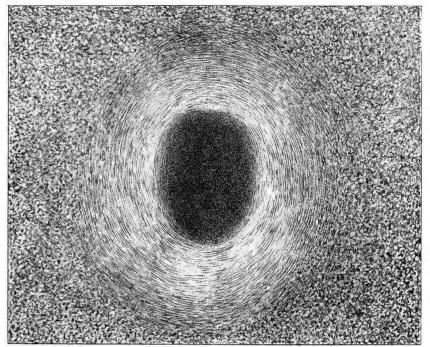


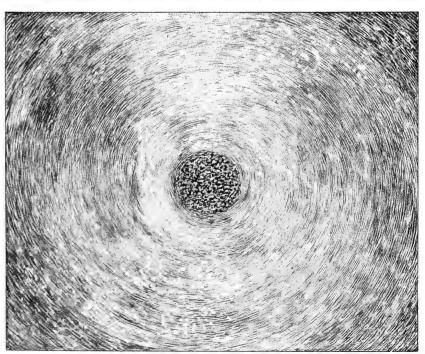






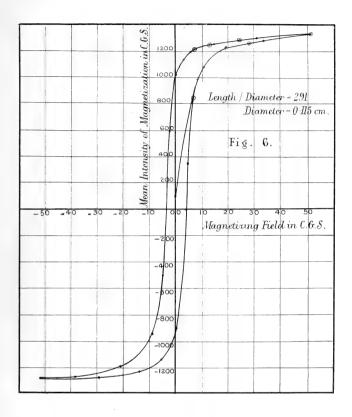


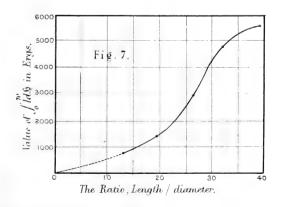




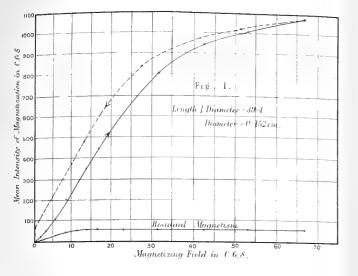
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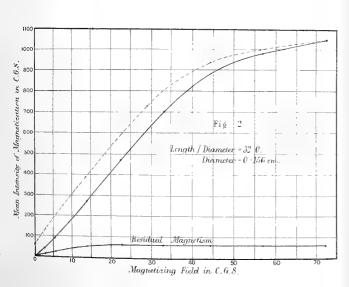


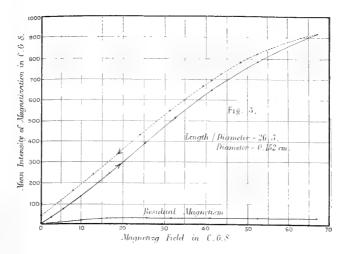


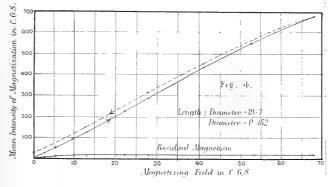


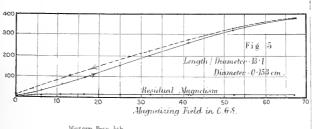


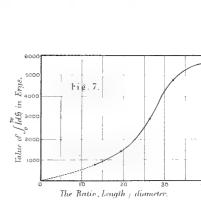


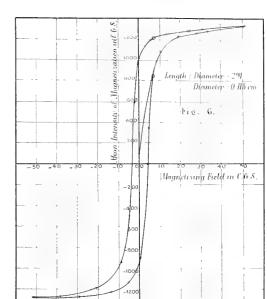




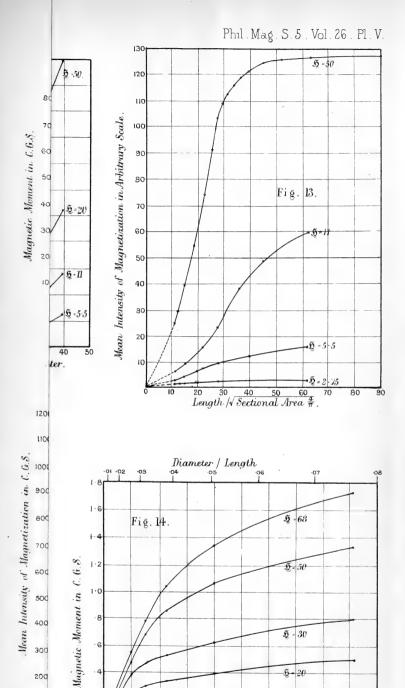












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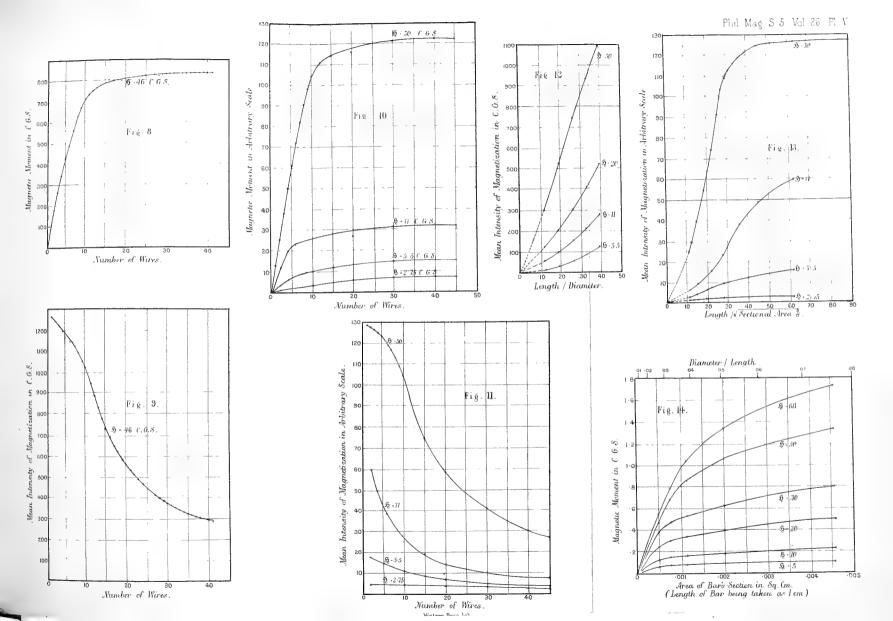
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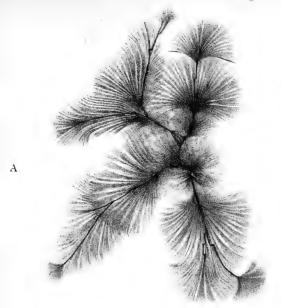
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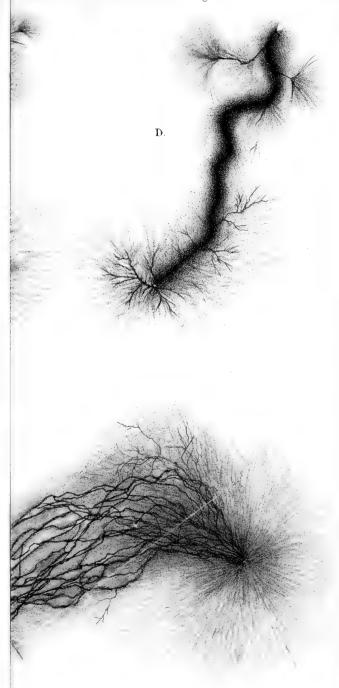




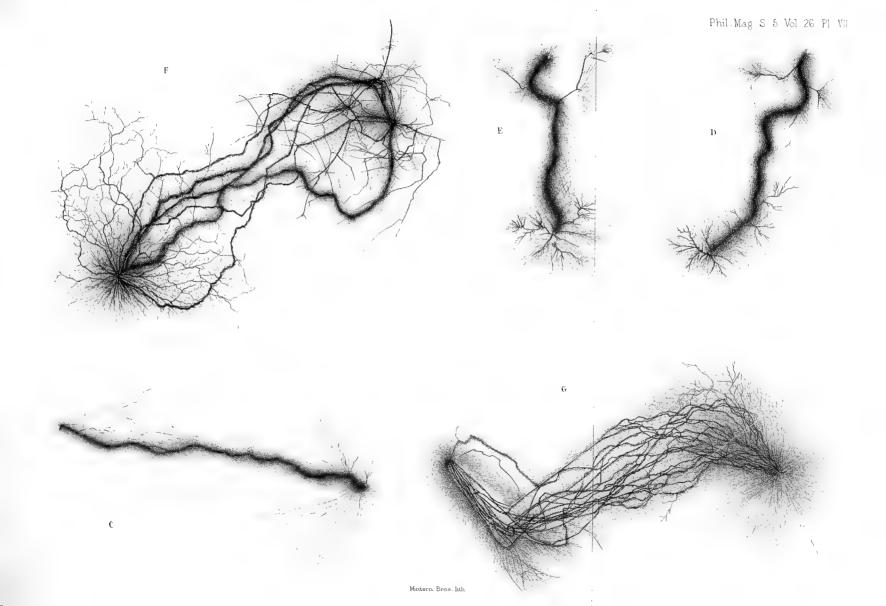
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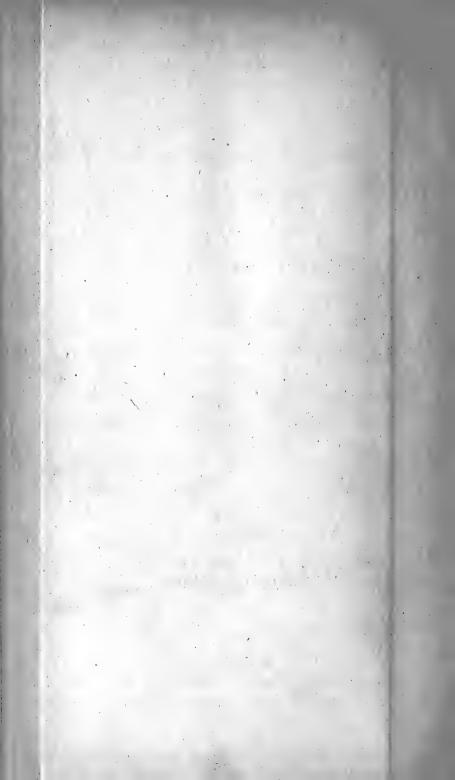


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